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# Heritage Science

# **RESEARCH ARTICLE**

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# Fading into the background: the dark space surrounding Vermeer's *Girl with a Pearl Earring*



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#### **Abstract**

The background of Vermeer's *Girl with a Pearl Earring* (c. 1665, Mauritshuis) has, until recently, been interpreted as a flat dark space. The painting was examined in 2018 as part of the research project *The Girl in the Spotlight* using a combination of micro- and macro-scale analytical techniques. The stratigraphy of the background was determined from samples mounted as cross-sections, and its material composition was analysed using electron microscopy and chromatographic techniques. The underlayer contains mainly charcoal black, and the glaze contains two organic colourants—indigo and weld—and a copper drier. Deterioration of the glaze has made features in the background difficult to discern with the naked eye. Complementary imaging techniques were able to visualise Vermeer's signature, and the suggestion of folded fabric (possibly a curtain) on the right side of the painting. The distribution of the layer(s) in the background were imaged using: infrared reflectography (900–1100 nm), multi-scale optical coherence tomography scanning, macroscopic X-ray fluorescence and 3D digital microscopy. Vermeer applied the black underlayer vigorously with overlapping brushstrokes that varied in thickness. When he applied the glaze on top, it levelled out to make a smooth flat surface. The visual effect of the background contrasts the figure of the *Girl* and projects her forward in space, closer to the viewer.

**Keywords:** Background, Glaze, Indigo, Weld, 17th century, Optical coherence tomography, Macroscopic X-ray fluorescence imaging, Focused ion beam-scanning transmission electron microscopy, Liquid chromatography

#### Introduction

Paintings by Johannes Vermeer (1632–1675) typically show figure(s) in an interior setting, with light filtered through a window on the left. Two 'tronies' (character studies) stand out within his oeuvre: Study of a Young Woman (c. 1665–1667, The Metropolitan Museum of Art, New York), and Girl with a Pearl Earring (c. 1665, in the collection of the Mauritshuis, The Hague, Fig. 1). The paintings are very similar in size, they were likely made around the same time, and are signed 'IVMeer' in the upper left. Both depict a young woman, strongly lit from the left, wearing a pearl earring. They are also the only known Vermeer paintings where a person is shown close-cropped, against a seemingly flat dark space.

In the Mauritshuis's *Girl with a Pearl Earring*, the contrast between the brightly lit figure and the surrounding dark background serves the important function of projecting the *Girl* forward in space, bringing her closer to the viewer and enhancing her three-dimensionality. Nowadays the background appears to have a mottled dark grey colour, but technical examinations of the painting have revealed that it has changed since Vermeer painted it.

The material composition of the background was first analysed by Kühn [1] in 1968, and has since been studied several times. To inform the conservators who restored *Girl with a Pearl Earring* in 1994, Groen, van der Werf, van den Berg and Boon investigated its composition and stratigraphy by examining and analysing samples mounted as cross-sections [2]. The samples revealed that the background was constructed with a black underlayer followed by a dark green translucent glaze layer. Groen et al. [2] concluded that background was originally an

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**Fig. 1** Johannes Vermeer, *Girl with a Pearl Earring*, c. 1665. MH670, Mauritshuis, The Hague. Polarised light photograph: René Gerritsen Art & Research Photography. Green: Samples taken from the background in 1968. Red: Samples taken from the background in 1994. Samples 26 and 34 are not indicated, since their precise sampling location is unknown. White box: Well-preserved glaze appears darker than surrounding paint. Blue box: Signature, see Fig. 7. Yellow box: Signature, see Fig. 8

"even, smooth, glossy, translucent, hard green paint, made to look darker and given depth by a dark underpaint." This resulted in a rich, translucent green color without distinguishing features.

In 2018, as part of the research project *The Girl in the Spotlight*, these samples were re-analysed using scientific techniques that have been developed or improved in the last decades: scanning electron microscopy—energy dispersive X-ray analysis (SEM—EDX), focused ion beam—scanning transmission electron microscopy (FIB—STEM), thermally assisted hydrolysis and methylation, pyrolysis gas chromatography—mass spectrometry (THM-Py-GC/MS), and ultra-high performance liquid chromatography with a photodiode array, attached to a fluorescence detector (UHPLC-PDA-FLR). Comparing the results of the analyses carried out over the last 50 years shows the evolution of analytical methods and how they have contributed to our understanding of the background.

The *Girl in the Spotlight* research team imaged the painting using complementary non-invasive methods. The brushstrokes and topography of the black underlayer were visualised using infrared reflectography and

multi-scale optical coherence tomography scanning (MS-OCT). MS-OCT also measured the thickness and distribution of the glaze layers. Macroscopic X-ray fluorescence (MA-XRF) mapped the distribution of elements in the glaze and revealed Vermeer's signature, which is barely visible to the naked eye in the upper left of the painting (Fig. 1: blue box). 3D digital microscopy was used to image the signature and layers in the background at  $1.1 \,\mu\text{m/pixel}$  ( $140 \times$  magnification).

#### **Experimental methods**

## Micro-sample analysis

### Paint micro-samples

During the conservation treatment of *Girl with a Pearl Earring* in 1994, microscopic samples from the background were mounted as cross-sections. They were embedded in Poly-pol PS230: a two-component polyester mounting resin (Poly-Service Amsterdam, The Netherlands). The methods used to examine them in the 1990s are described in Appendix 2 of Groen et al. [2].

Samples 19 and 21 were taken from the lower right corner of the painting (Fig. 1). In 2017–2018, the cross-sections of samples 19 and 21 were analysed using light microscopy and SEM–EDX. Small fragments of sample 19 preserved on a microscope slide were examined in transmitted light. Fragments of sample 21 were analysed using UHPLC-PDA-FLR.

The stratigraphy and composition of samples 26 and 34 show that they are from the background, but their precise original location is unknown (see legend of Table 1). Sample 26 was photographed in transmitted light, but not reanalysed for this study. The cross-section of sample 34 was analysed using light microscopy, SEM–EDX, FIB–STEM and Fourier transform infrared spectroscopy–attenuated total reflectance spectroscopy (FTIR–ATR: results not shown here).

### Light microscopy

The cross-sections taken in 1994 were re-photographed in 2009 using a Leica DM2500 light microscope equipped with a Leica DFC490 digital camera. In 2018, a Zeiss Axio Imager.A2 m microscope equipped with a Zeiss AxioCam MRc5 digital camera was used to re-examine the cross-sections—and to photograph samples 19 (dispersion) and 26 (thin section) in transmitted light—at spatial resolutions of 0.54  $\mu m/pixel~(100\times), 0.27~\mu m/pixel~(200\times)$  and 0.11  $\mu m/pixel~(500\times)$  in bright field, dark field and ultraviolet (UV-A).

# Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX)

SEM backscattered-electron images of the uncoated samples were acquired at the *Ateliergebouw* (Studio Building),

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Table 1 Samples from the background of Girl with a Pearl Earring

Sample number	Sample type <sup>a</sup>	Location on the painting: (Fig. 1)	Previous analyses: 1968: Kühn [1] 1998: Groen et al. [2], Appendix 2	Analysis 2017–2019	
5	В	Dark paint, probably from back- ground	1998: LM of cross-section	THM-Py-GC/MS of fragments	
19	Α	Background	1998: LM, SEM-EDX of cross-section	LM, SEM-EDX of cross-section (Fig. 2)	
21	A	Background	1998: LM, SEM–EDX, FTIR of cross- section; microchemical test of fragments	LM, SEM-EDX of cross-section (Fig. 3); UHPLC of fragments	
26	В	Probably background	1998: SEM-EDX of cross-section; cross-section prepared as thin- section, FTIR of thin-section; HPLC and wet chemical tests of fragments	LM of thin section in transmitted light	
34	В	Probably background	1998: LM of cross-section; DTMS and Py-TMAH-GC/MS of fragments	LM, FIB–STEM, FTIR–ATR of cross- section (Fig. 4)	
Hg. 11	Α	Right edge, near lower right corner	1968: LM, ESA of cross-section	_	
Hg. 12	Α	Left edge	1968: LM, ESA of cross-section	_	

<sup>&</sup>lt;sup>a</sup> 'A' samples were those sampled from a known location in 1968 or during the 1994 treatment. 'B' samples are dislodged fragments that became stuck to the surface in an unrelated part of the painting, and were preserved as sample material. Based on the stratigraphy, pigment composition, and comparison to other samples, an educated guess could be made as to the general area they originated from. For a complete list of 'A' and 'B' samples re-examined in 2017–2019, see [9], Appendix S1

Amsterdam, with an FEI NovaNano SEM 450 variable pressure electron microscope operated at low vacuum (70 Pa), and an accelerating voltage of 20 kV. The SEM was equipped with a ThermoFisher NSS EDX system to yield elemental composition of the pigments within the layers.

EDX mapping was done at Shell Technology Centre Amsterdam (STCA) using a JEOL 7000F high-vacuum SEM coupled to a ThermoFisher NSS EDX system with dual 30 mm² silicon drift detectors. The samples were carbon-coated (Leica ACE600 nominally 15 nm thick) prior to EDX mapping to improve surface conductivity. All the samples were mapped using spectral imaging at either 500× or  $1000\times$  magnification. Each map consists of  $256\times202$  pixels and the collection time was typically 30 min. The step size of the images was  $1.04~\mu\text{m/pixel}$  and  $0.52~\mu\text{m/pixel}$  for the  $500\times$  and  $1000\times$  images, respectively.

# Focused ion beam-scanning transmission electron microscopy (FIB-STEM)

The combination of STEM and EDX were used to 'map' the element distribution in thin sections prepared from painting cross-sections using the FIB. The thin sections were prepared using the standard ex situ lift-out method [3]. This involves cutting out a cross-section specimen from its substrate and transferring this onto a thin support membrane using a micromanipulator. In the case of paint cross-sections this means that the section can be milled directly from the bulk sample. All thin sections were prepared using a FEI Helios dual beam system. The rough milling was done using a beam current of 21 nA

and for the final polishing it was 93 pA. The tilt off-set was  $0.6^{\circ}$ . The nominal thickness of the sections was 200 nm with a width of 20  $\mu$ m and height of 8  $\mu$ m.

Spectral images were made at resolutions ranging from 26 nm/pixel  $(20,000\times)$  up to 2.2 nm/pixel  $(240,000\times)$  with an accelerating voltage of 200 keV. Each map consists of  $512\times512$  pixels and the collection time was typically between 5 and 15 min. The microscope used for this work was a JEOL2800 with two Centuro EDX silicon drift detectors. The measurements were made at the Shell Technology Centre Amsterdam (STCA).

# Ultra-high performance liquid chromatography with a photodiode array, attached to a fluorescence detector (UHPLC-PDA-FLR)

Samples were analysed by means of ultra-high-performance liquid chromatography (UHPLC) with a photodiode array (PDA,  $\lambda = 200-800$  nm), attached to a fluorescence detector (FLR,  $\lambda_{em} = 510$  nm,  $\lambda_{ex} = 580$  nm).

The samples were photographed with a digital microscope and then transferred to glass micro-vials. Extraction was carried out with a 15  $\mu L$  solution of hydrochloric acid (36% technical—Acros), water (Millipore) and methanol (LC–MS grade—Honeywell) in 2:1:1 ratio, respectively. The extraction was vortexed for 8 s and heated in a water bath at 100 °C for 10 min. The sample was then evaporated under a gentle nitrogen flow (30 min). When dry, the sample was solubilised with 16  $\mu L$  of dimethyl sulfoxide (DMSO—Sigma Aldrich), the micro-vial was briefly vortexed and then centrifuged at 90 G for 5 min.

The chromatography apparatus used was a Waters® ACQUITY UPLC H-Class System. The column was a

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C18, 15 cm BEH (ethylene bridged hybrid) column with a pre-filter, used to separate the colourants with a solvent gradient of: (a) 10% methanol in water, (b) 100% methanol and (c) 1% formic acid. 5  $\mu$ L of the extracted samples were injected into the column with an auto sampler [4].

# Thermally assisted hydrolysis and methylation, pyrolysis gas chromatography–mass spectrometry (THM-Py-GC/MS)

The Py-TMAH-GC/MS method used by Groen et al. [2] in the 1990s is based on the same procedure of hydrolysis and methylation as the recent THM-Py-GC/MS analysis [5]. Fragments from Sample 5 were made into a suspension with a few drops of a 5% solution of tetramethylammonium hydroxide in methanol, and the solvent/ suspension was transferred to a pyrolysis cup. The sample was pyrolysed using a high-speed temperature range starting at 360 °C, raised to 660 °C. Through the combination of the heat and the reagent, pyrolysis, hydrolysis and/or methylation took place in the fatty acids, the resin acids and the polymer fraction of the sample. The total component mixture was separated by GC and the separated components were detected and identified with MS. The pyrolysis unit used was a Frontier Lab 3030D pyrolyser mounted on a Thermo Scientific Focus GC/ISQ mass spectrometer combination. Separation took place on an SLB-5 ms (Supelco) capillary column with a length of 20 m, an internal diameter of 0.18 mm and a film thickness of 0.18 µm. Helium was used as the carrier with a constant flow of 0.9 mL/min. The split ratio was set to 1:30. The temperature program used was 35 °C, held stable for 1 min, raised with 60 °C/min to 110 °C, raised with 14 °C/min to 240 °C, raised with 5 °C/min to 315 °C, held stable for 2 min. The column was directly coupled to the ion source of the mass spectrometer. The temperature of the interface was 250 °C, and the temperature of the ion source was 220 °C. Mass spectra were recorded from 29 to 600 amu with a speed of 7 scans per second.

#### Non-invasive imaging

# Technical photography: Polarised light photography, and digital infrared reflectography (900–1100 nm)

The camera body was a Hasselblad 503CX, with a digital camera back: Leaf Credo 80 WS (wide-spectrum) with an 80 MP CCD sensor, sensitive from 380 nm to 1100 nm. The exposure settings for most images were: ISO 35, exposure time 1/60 s, and aperture f/11. The lens was a Carl-Zeiss 120 mm macro-planar lens. For infrared reflectography, a Heliopan digital RG 1000 filter was placed in front of the lens, which cuts off wavelengths below 900 nm. For polarised light photography, a TG1 and circular polarising filter were placed in front of the lens, and polarising foil was positioned in front of the lamps. The light sources used were Broncolor strobes

with 640 W halogen modelling lights. Two P70 reflector shells were used.

For the infrared reflectogram, the whole painting was photographed both as a single image (output 16-bit, eciRGB v2 ICCv4, 430 MB, 7760  $\times$  9300 pixels) corresponding to an on-painting spatial resolution of 50  $\mu m/$  pixel, and at a higher resolution of 16  $\mu m/$  pixel in the form of sixteen images (output 16-bit, eciRGB v2 ICCv4, 4.5 GB,  $25,850\times31,000$  pixels) that were stitched and precisely registered to the whole-painting overview image. Calibration was done with X-rite ColorChecker digital SG, with BasICColor 3 profiling. Capture One software was used to capture images, using a custom camera profile, and creating an LCC-lens profile, output 16-bit eciRGB v2 ICCv4. BasICColor input 3 was used to create a custom camera profile. Photoshop CC was used for end (final) corrections.

#### Macroscopic X-ray fluorescence (MA-XRF)

Macroscopic X-ray fluorescence maps of the entire painting were collected in two scanning sessions using the Bruker M6 Jetstream [6]. The instrument consists of a measuring head equipped with a 30 W rhodiumtarget microfocus X-ray tube, a polycapillary lens, and a 60 mm<sup>2</sup> XFlash silicon drift detector (SDD) with a beryllium window (energy resolution < 145 eV at Mn- $K_{\alpha}$ ). By slowly moving the measuring head on the XY-motorised stage, the painting is scanned pixel by pixel, line by line. By recording the emitted X-ray fluorescence radiation, the chemical elements present in the paint (associated with specific pigments) can be identified. With the Bruker M6 Jetstream, only elements heavier than silicon can be detected. Scans were carried out at 50 kV and a current of 600 µA, with a 400 µm step size, and a dwell time of 125 ms. The distance between the scanning head and the paint surface was set at approximately 1 cm, corresponding to an X-ray spot size of circa 300 µm. All data were collected with the Bruker M6 Jetstream software package. The acquired data cubes were then exported as raw files and processed and stitched using PyMca and Datamuncher software [7].

#### Multi-scale optical coherence tomography (MS-OCT)

MS-OCT scanning was performed with a Thorlabs Ganymede-II-HR spectral-domain OCT system, which was combined with XYZ-scanning stages. The system was operated with custom built Labview software. The OCT system has a source spectrum centred at 900 nm, spanning a bandwidth of 195 nm. The MS-OCT setup has a depth resolution in the Z-direction of 3  $\mu$ m in air. The XY plane was sampled anisotropically with a sampling rate of 8.5  $\mu$ m/pixel in the scan direction and 67.6  $\mu$ m/pixel in the lateral direction. Although the

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MS-OCT system is capable of spatially sampling at an isotropic resolution of 12 µm/pixel, the increased data size related to sampling at this resolution was deemed unnecessary for this project. The OCT system was operated with a Thorlabs LSM04-BB telecentric imaging lens that has a maximum field of view of  $14.1 \times 14.1 \text{ mm}^2$ . The computer was a Dell precision workstation (T1700) with 16 GB RAM memory, an Intel Xeon E3-1271v3 processor and an added internal 1 TB solid state drive (SSD) (WD Blue 3D NAND) for data storage during measurements [8]. For large area scanning, the OCT scan probe was mounted on a 3-axis stage consisting of two 20 cm (X and Y-axis) scan range stages (8MT50-series, Standa) and a 10 cm (*Z*-axis) scan range stage (8MT50-series, Standa) mounted in an XYZ configuration. The Z-stage regulates the distance between the OCT's telecentric scan lens and the painting's surface, by autofocusing every volume scan. Without this operation, the object would be out of focus due to the small imaging depth (1.89 mm) of the OCT system. The OCT probe head was mounted to the setup with the aid of a customised mount. The maximum dimension of the scanned surface (limited by the scanning stages) was  $20 \times 20$  cm, therefore Girl with a Pearl Earring was scanned in four sections. The top edge was not scanned in its entirety.

#### High-resolution 3D digital microscopy

Key areas of the painting were examined using a 3D digital microscope Hirox RH-2000 with a MXB-5000REZ lens, at resolutions of 4.4  $\mu m/pixel~(35\times)$  to 0.03  $\mu m/pixel~(5000\times)$ . Raking light was used to minimise reflections and visual interference from the varnish. The painting was placed in a horizontal position surrounded by a motorised 'bridge' stand with a  $500\times500$  mm motorised XY axis. The lens was placed on a 30 mm motorised Z-axis focus block.

The selected area (the "M" within Vermeer's signature) was automatically scanned using high-resolution 3D stitching at a sampling resolution of 1.1  $\mu$ m/pixel (140× magnification/field of view: 2.1×1.31 mm) using the motorised XYZ-axis: the microscope acquired a series of images in the Z-axis, capturing each focused layer individually and then combining them in one single all-infocus image (also known as Z-stacked or extended depth of field). The microscope then automatically moved in the XY-direction to the next tile, and the process started again. The result for each tile is a Z-stacked image as well as a TDR file (Hirox 3D file format) which includes true colours as well as altitude, so that the XYZ coordinates are registered for each pixel.

In total, 700 individual Z-stacked 3D files were acquired with a 30% overlap, resulting in a 3D stitched image of  $30 \times 32$  mm in XY and 0.45 mm in Z (total max–min after

levelling). The total resolution for this stitched image is 810 million pixels which was then reduced to 25% in X and Y (1/16th of the pixel size) for easy processing and measurement of the 3D file.

The Hirox RH-2000 main unit software was used to calibrate and display a live image, then to create full auto *Z*-stacked 3D data using a motorised *Z*-axis, and to program a fully automatic *XYZ* acquisition. The software was modified specifically for the *Girl in the Spotlight* project, allowing *XYZ* stitching with selectable overlap without any pixel size limit, with offline processing. The single 3D images were then stitched using the Hirox E-tiling software and measured using Digital Surf Mountains Map 8.

#### Results

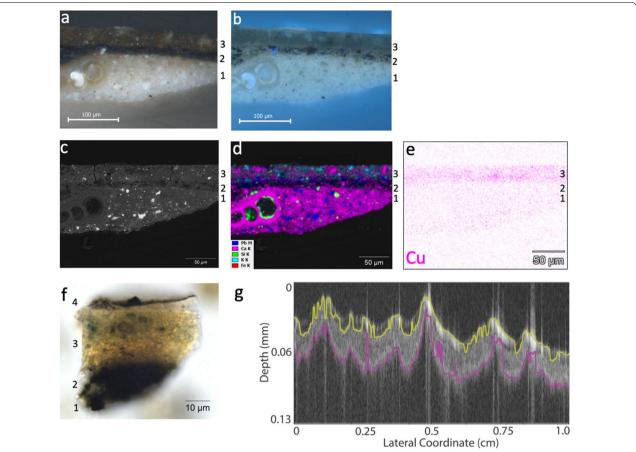
### Stratigraphy and material composition of the background Stratigraphy

The background of Girl with a Pearl Earring has a simple stratigraphy. Seven samples from the background have been studied over the last 60 years (Fig. 1 and Table 1) [1, 2, 9]. Cross-sections show that it is built up from two distinct layers (Figs. 2, 3, 4). On top of the light warm grey ground, Vermeer applied black paint, approximately 10-25 µm thick (measured from four cross-sections examined using light microscopy). The straight interface between this underlayer and the one above it suggests that Vermeer left it to dry before applying a semi-translucent glaze layer on top. This glaze is approximately 20-25 µm thick, as averaged from measurements made from four cross-sections. It appears greenish in a sample from the left of the painting, and yellow-brown in samples from the lower right. In transmitted light, the matrix of the glaze appears yellowish, with some indistinct blue spots within it (Fig. 2f).

#### Black underlayer

The studies by Kühn [1] and Groen et al. [2] had attempted to characterise the materials present in the underlayer and glaze in the background of Girl with a Pearl Earring, but some results were inconsistent. The materials in the paint and ground layers of Vermeer's paintings were first systematically studied in 1968 by Kühn [1]. He took two samples along the left and right edges (Fig. 1), examined them as cross-sections under a microscope, and analysed their elemental composition using emission spectrographic analysis (ESA). Kühn described the underlayer as "charcoal black." As part of the technical examination connected with the 1994 restoration treatment of Girl with a Pearl Earring, four samples from the background were mounted as crosssections. Groen et al. determined that the underlayer was made of bone black within a brownish medium [2].

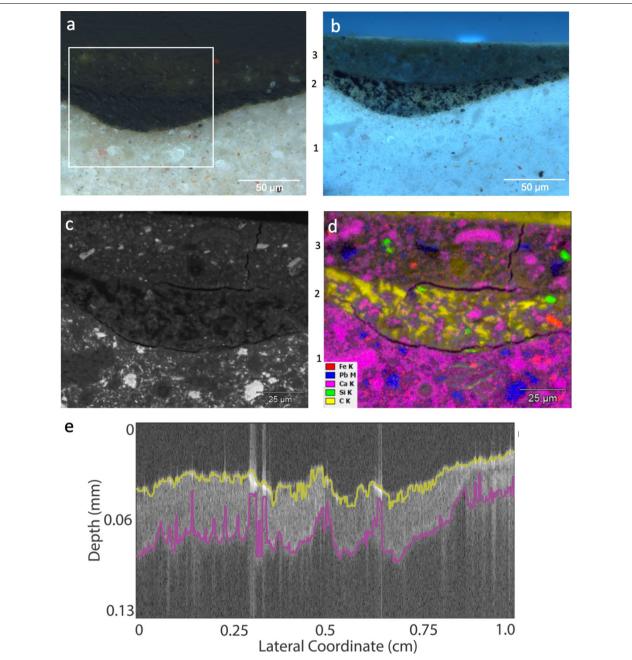
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**Fig. 2** Sample 19 from the background in the lower right: **a** Light microscopy of cross-section, bright field. 1: ground, 2: underlayer, 3: glaze. **b** Light microscopy of cross-section, UV fluorescence. **c** SEM backscatter image of cross-section. **d** SEM–EDX map of cross-section: Pb (blue), Ca (magenta), Si (green), K (teal), Fe (red). **e** SEM–EDX map of cross-section: copper (Cu). **f** Light microscopy of a fragment in dispersion, transmitted light. 1: ground, 2: underlayer, 3: glaze, 4: (restoration) varnish and dirt. Image: Guusje Harteveld. **g** MS-OCT B-scan close to the location of Sample 19, with segmentation indicated for: glaze–underlayer interface (purple) and air–varnish interface (yellow). Lateral scale here is different from other parts of this figure

Three of the cross-sections taken from the background in 1994 were re-examined prior to and during the 2018 project The Girl in the Spotlight: samples 19 (Fig. 2) and 21 (Fig. 3) taken near the lower right corner, and sample 34 where the precise sampling location is unknown (Fig. 4, and Table 1). The 2018 examination confirmed the presence of charcoal, but did not identify bone black in the underlayer. Under the light microscope, the majority of the black material consists of splintery particles that closely resemble charcoal, especially when examined in UV fluorescence under high magnification (Figs. 3b, 4b: layer 2). Elemental mapping of Sample 34 with SEM-EDX identified carbon (C) in the splintery particles (Fig. 4c). Other particles in the layer appeared to contain calcium (Ca), iron (Fe), and/or aluminium (Al). To identify these particles, the underlayer was examined and mapped at a higher magnification and resolution using FIB-STEM (Fig. 4e, f). Within the charcoal-rich layer, FIB-STEM detected distinct particles containing only calcium (Ca), suggesting the presence of chalk; or both calcium (Ca) and sulphur (S) in a ratio that suggests gypsum. Although small amounts of phosphorus (P) were detected in the black underlayer, no particles containing the combination of calcium (Ca), phosphorus (P) and magnesium (Mg) were detected, ruling out the presence of bone (or ivory) black. Other dispersed particles within the underlayer suggested the presence of alum: they contained aluminium (Al), potassium (K) and sulphur (S). The combination of these recent analyses of cross-sections shows that the underlayer is composed primarily of charcoal, and contains a relatively small amount of chalk, gypsum, an earth pigment, and possibly alum (associated with a lake pigment).

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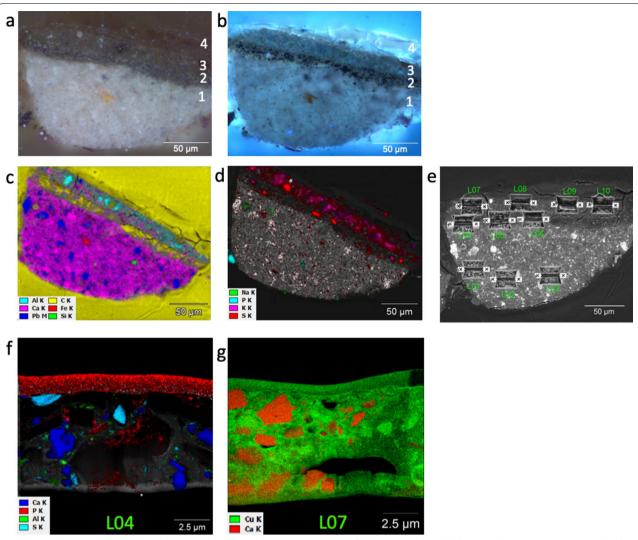
**Fig. 3** Sample 21 from the background in the lower right: **a** Light microscopy, bright field, ×400. 1: ground, 2: underlayer, 3: glaze, with a white box indicating the location of **c**, **d**. **b** Light microscopy, UV fluorescence, ×400. **c** SEM backscatter image, area indicated with white box on **a**. **d** SEM–EDX map: Fe (red), Pb (blue), Ca (magenta), Si (green), C (yellow). **e** MS-OCT B-scan close to the location of Sample 21, with segmentation indicated for: glaze–underlayer interface (purple) and air–varnish interface (yellow). Lateral scale here is different from the other parts of this figure

### Green glaze

The components of the glaze were analysed in all three studies, with some inconsistencies noted between the 1968 and 1998 analyses. Kühn described the glaze as a green-brown layer containing umber, lead white and verdigris. It is notable that ESA analysis showed a strong

signal for copper (Cu) and aluminium (Al), along with other elements. Kühn analysed organic components of ground and paint layers from other paintings by Vermeer using microchemical tests, but apparently no tests were possible on the two samples he took from *Girl with a Pearl Earring* [1].

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**Fig. 4** Sample 34, precise sampling location unknown: **a** Light microscopy, bright field, 1: ground, 2: underlayer, 3: glaze, 4: (restoration) varnish. **b** Light microscopy, UV fluorescence. **c** SEM–EDX map: Al (teal), Ca (magenta), Pb (blue), C (yellow), Fe (red), Si (green). **d** SEM–EDX map: Na (green), P (teal), K (magenta), S (red). **e** Backscatter image showing FIB lamella locations. **f** STEM-EDX overlay of FIB lamella LO4 from layer 2 (underlayer): Ca (blue), P (red), Al (green), S (teal). **g** STEM–EDX overlay of FIB lamella LO7 from layer 3 (glaze): Cu (green), Ca (red)

In the 1990s, the inorganic components of the glaze were analysed using SEM-EDX and Fourier transform infrared spectroscopy (FTIR) of cross-sections. Groen et al. [2] found that it contained a significant amount of calcium (Ca) and aluminium (Al): two elements associated with inert substrates for organic pigments, such as yellow or red lakes. Other inorganic components that they identified in the glaze were: chalk, lead white, earth pigments and a small amount of black pigment. No verdigris or other copper-containing pigments were mentioned. Sample 26 was made into a thin-section—which showed how transparent the green glaze is (illustrated in Groen et al. [2])—and some fragments were used for

micro-destructive analyses. To identify the organic components of the glaze, samples were analysed using wet chemical analysis, high performance liquid chromatography (HPLC) and direct temperature-resolved mass spectrometry (DTMS). Groen et al. found two dyestuffs in the glaze: luteolin—the yellow colouring matter of weld, and indigotin—the blue colourant in indigo (described below) [2].

The 2017–2018 re-examination of the samples clarified the inorganic and organic components of the glaze. The organic components of the glaze were reanalysed using two fragments from sample 21 that had been preserved in 1994, but not embedded as cross-sections. Liquid Vandivere et al. Herit Sci (2019) 7:69 Page 9 of 19

chromatography (LC) confirmed the presence of luteolin and indigotin in the glaze, and detected more components: apigenin, luteolin methylether, luteolin glycoside, apigenin glucoside, and unidentified minor flavonoids. This confirmed the findings from 1998: that the yellow pigment is made from weld, and the blue colourant is indigo. Weld pigment is prepared from the plant Reseda luteola L., also known as dyer's rocket. The plant is rich in luteolin: a tetra-hydroxy-flavone with a bright yellow colour. Because weld is a soluble dyestuff, the colourant must be precipitated onto a substrate to be used as a pigment, whereas indigo is insoluble and does not need a substrate [2]. Indigo is a deep blue pigment produced from glycosides of indoxyl-rich plants belonging to the Indigofera, Cruciferae, Polygonaceae or Apocynaceae family [10].

SEM-EDX mapping of sample 34 showed the presence of: aluminium (Al), calcium (Ca), lead (Pb), iron (Fe), potassium (K), sulphur (S), phosphorus (P) and sodium (Na) (Fig. 4c, d). Remarkably, SEM-EDX detected a very small amount of dispersed copper in the glaze of sample 19 from the lower right corner of the painting (Fig. 2e). Copper had been noted in 1968 (Kühn suggested it was verdigris [1]), but not mentioned by the 1994 researchers [2]. FIB-STEM of the glaze in sample 34 showed that calcium is isolated to specific particles—suggesting the presence of chalk, and in combination with sulphur (S) suggesting the presence of gypsum—while the copper is homogenously distributed in the spaces between these particles (Fig. 4g). No distinct copper-rich particles are visible, as the copper was dispersed down to a 10 nm scale. It is only present in a small quantity: approximately 1% by weight in the glaze layer of the cross-section.

The chalk, gypsum, potassium compound (probably present as sulphate), and the aluminium compound (probably present as oxide or hydroxide) are probably related to the substrate of the weld; Groen et al. [2] refer to the 1620 manuscript by de Mayerne, who specified that the yellow dye should be precipitated onto alum, then kneaded with chalk [11]. De Mayerne also mentioned adding alum to paint containing organic pigments to make it glossier and more durable. Alternatively, chalk and/or gypsum could have been used as a bulking agent or absorbent for an organic pigment [2]. A tiny amount of lead white was also detected in the glaze layer: additional analysis using macroscopic X-ray powder diffraction (MA-XRPD) revealed that the lead white was cerrusiterich [12]. The copper- and lead-based pigments and the earth pigments in the glaze would have helped it to dry faster, and would presumably have had limited effect on the colour and translucency of the glaze [13]. The very small amount of copper is distributed throughout the glaze, and its precise origin is unclear. It is possible that Vermeer added a small quantity of verdigris to the paint, which then dissolved in the medium [10]; alternatively, the oil used as a binding medium might have been heated in a copper pot [11].

#### Binding medium

In the current study and the 1998 publication by Groen et al. [2], gas chromatography—mass spectrometry analyses were used to characterise the binding medium of *Girl with a Pearl Earring*, and to identify non-original (restoration) materials. Of the five samples that have been analysed, two are probably from the background: samples 5 and 34 were displaced fragments that had become stuck to the painting's surface in an unrelated location, then were carefully removed and preserved as sample material during the 1994 treatment (Table 1: 'B' samples) [2, 9]. Other fragments from samples 5 and 34 were also prepared as cross-sections; their stratigraphy and pigment composition under the light microscope resembled samples known to have been taken from the background.

Sample 34 contained primarily original materials: presumably the ground, underlayer and glaze from the background. Groen et al. [2] analysed the whole sample using pyrolysis-tetramethylammonium hydroxide-gas chromatography mass spectrometry (Py-TMAH-GC/MS). Linseed oil, was identified, based on a palmitic acid/stearate acid (P/S) ratio of 1.7, and a relatively high C8/C9 diacid concentration (C8/C9 ratio not specified) [2, 14].

In 2018, small fragments of Sample 5 were analysed using thermally assisted hydrolysis and methylation, pyrolysis gas chromatography-mass spectrometry (THM-Py-GC/MS) (Table 1) [5, 15]. Before analysis, the light-coloured fragments (presumably the ground) were separated from those containing a black paint layer (presumably the underlayer from the background) so that they could be analysed separately. The light-coloured fragments from the ground contained mostly heat-bodied linseed oil [16]. In the sample from the black paint layer, the highest proportion of material was identified as (slightly) heat-bodied linseed oil with P/S ratio of 1.5 (after correction for both skin grease and beeswax), and a C8/C9 diacid ratio of 0.32. Raw linseed oil generally has a C8/C9 diacid ratio of 0.2, whereas heat-bodied linseed oil (depending on the rate of heating) shows ratios ranging between 0.4 and 0.8. Surprisingly, THM-Py-GC/MS also detected rapeseed oil, from the plant Brassica napus as a small addition to the linseed oil (1-2% as compared to the linseed oil) [17]. Restoration materials applied before the 1994 treatment, and a large amount of sulphates and phosphates were also detected [2, 9].

The analyses from the 1990s and 2018 complement one another. The analysis of the 1990s identified the binding medium as linseed oil, and the recent analysis suggested Vandivere et al. Herit Sci (2019) 7:69 Page 10 of 19

Table 2 Layer thicknesses (µm)

Layer	Cross-section: Sample 19	B-scan near Sample 19	Cross-section: Sample 21	B-scan near Sample 21	Cross-section: Sample 34
Varnish	_	29.72	_	33.51	20
Glaze	25		20-30		20
Underlayer	10-24	-	10	_	10-20

Thickness range measured from cross-sections, compared to average MS-OCT physical thicknesses (corrected to refractive index of 1.5) from B-scans made near the sample sites

that the linseed oil—at least the one in the ground and to bind the dark paint layer—had been heated. The possible effect of heating on the handling properties of the paint is described below. There is no specific information about the binding medium of the glaze: it was analysed along with the rest of sample 34 [2], but might not have been present in sample 5.

#### Varnish

Although it is possible that Vermeer applied a varnish to *Girl with a Pearl Earring* after painting, no remains of an original varnish layer have been detected. Most 17th-century paintings have undergone several cleaning cycles in the course of time, where the old varnish was removed, and a new varnish was applied. The (remains of) surface coatings visible in cross-sections are non-original varnishes applied during various conservation/restoration treatments. Cross-sections 19 and 21 have only tiny remnants on the surface (Figs. 2b, 3b), because the samples were probably taken during varnish removal or after the painting had been cleaned.

A surface coating up to 20  $\mu$ m thick is visible on sample 34, and probably comprises several campaigns of restoration varnish (Fig. 4b: layer 4). This cross-section was a fragment that had become stuck to the painting's surface and was carefully removed in 1994; it includes layer(s) of restoration varnish that are no longer present on the painting. After removing old varnish layers during the 1994 treatment, the conservators applied two thin layers of dammar varnish [18], which are still present on the surface of the painting today.

#### Layer thicknesses

The thicknesses of layers in the background of *Girl with a Pearl Earring* were determined using two methods: using a digital scale bar to measure cross-sections examined using light microscopy and SEM–EDX, and from 'B-scans' produced using multi-scale optical coherence tomography (MS-OCT). A comparison between the values from these two techniques is reported in Table 2.

Multi-scale optical coherence tomography, one of the scanning techniques used during the 2018 technical

examination, allowed measurement of the thickness of Vermeer's original glaze layer and the varnish layers that were applied in 1994. MS-OCT is a non-contact and non-destructive imaging technique capable of imaging semi-translucent 3D volumes of thin layered structures up to a few millimetres deep at high spatial resolution [19, 20]. The wavelength of the OCT source spectrum (centred at 900 nm) is absorbed by the carbon-based charcoal underlayer. The semi-translucent layers detected using MS-OCT can be visually represented as a B-scan: a 'virtual cross-section' that shows the interfaces between layers with different optical scattering properties (such as refractive index). The interfaces are obtained by segmenting the MS-OCT data with a graph-based method [8]. In Figs. 2g and 3e, the air-varnish interface (yellow) and the glaze-underlayer interface (purple) are clearly distinguishable. The varnish is too thin to be segmented separately from the glaze because its thickness is in the range of axial resolution of the OCT system; for this reason, the thickness of both (semi-)translucent layers—the varnish and the green glaze—are reported together. The 'glaze + varnish thickness' is obtained by subtracting the depth of the glaze-underlayer interface from the air-varnish interface.

In scientific literature about OCT, thicknesses in a B-scan are usually expressed in terms of their optical path length, which do not take into account the effect of the refractive index of the different materials [19]. In this paper, in order to be comparable with the paint cross-sections directly, the B-scan measurements are expressed as 'physical thicknesses' in micrometres (µm). To calculate the physical thickness, it is assumed that the glaze and varnish both have a refractive index of approximately 1.5; the refractive index for linseed oil can range between 1.48 and 1.57 [20]. The actual refractive index of the glaze and varnish layers in *Girl with a Pearl Earring* is difficult to determine quantitatively because the glaze is not homogeneous: it contains several pigments and colourants, some of which have degraded.

The physical thickness of the glaze + varnish measured in the MS-OCT B-scans were compared to the thicknesses of the semi-translucent layers measured from the cross-sections taken from the painting. The B-scans

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were imaged along a line of 1.0 cm, in the vicinity of the sample sites where the cross-sections were sampled. The values show that the B-scan thickness measurements correlate fairly accurately with the range of thicknesses in the four samples embedded as cross-sections; they are slightly higher (Table 2).

The slight differences between the thicknesses determined from the cross-sections and the B-scans can be due to several factors. Firstly, the varnish layers applied towards the end of the treatment in 1994 were measured using MS-OCT, but were not yet present on the surface when the cross-sections were taken. Secondly, the MS-OCT data is based on a lateral slice across 1.0 cm (10,000  $\mu m$ ) of the painting's surface. This provides more representative thickness information than a conventional paint cross-section, which only provides a highly localised measurement of thickness in a single area: here, approximately 200–300  $\mu m$  wide. MS-OCT can also map the distribution of the semi-translucent layers over a large surface of the painting as a glaze + varnish thickness map (see below).

### Distribution of the layers in the background

As part of the 2018 technical examination *The Girl in the Spotlight*, several imaging techniques were used to map the underlayer and glaze of *Girl with a Pearl Earring*: polarised light photography, infrared reflectography (900–1100 nm), MS-OCT, MA-XRF and 3D microscopy.

#### Technical photography

Polarised light photography captured more details in the background than a 'normal light' photograph. Polarisation reduced the reflections from cracks and showed the colour differences in the background (Fig. 1). Overall, the background is a patchy greyish-green, but an area to the left of the *Girl*'s mouth (indicated with a white box in Fig. 1) appears darker and more saturated: this is an area that was covered by overpaint, but exposed during the 1994 treatment when overpaint was removed ([2], discussed below). The lower right corner is slightly warmer and more reddish in tone, and the upper right corner has some diagonal lines that are slightly lighter or darker than the rest of the background.

Infrared reflectography (900–1100 nm) showed the distribution of the black underlayer. Charcoal black (identified in the samples) is a carbon-based pigment that absorbs infrared, and can therefore be detected using this method [21]. The infrared image shows that the underlayer is rather evenly distributed under the whole background of the painting (Fig. 5b). Vermeer's brushstrokes are visible, especially to the left of the figure, where they

are haphazard, often diagonal and overlapping to completely cover the space. Along the upper edge, he seems to have applied horizontal brushstrokes more carefully to keep the paint within the perimeter (Fig. 6a). Along the right side of the composition, the distribution of carbon black is not as even: the bottom right corner is lighter (with less carbon-based black), and some diagonal lines are visible in the upper right corner (Figs. 5d, 6a). These were a first indication that the background might not be as uniform and monochrome as it seems to the naked eye.

#### Multi-scale optical coherence tomography (MS-OCT)

The MS-OCT glaze+varnish layer thickness map shows that the glaze is distributed over the entire surface of the background (Fig. 5c). The varnish evenly covers the whole surface (including the figure), but it was too thin to be automatically segmented. The overall thickness of the semi-translucent layers in the background is in the range of 30–40  $\mu m$ , based on physical thicknesses with the refractive index assumed to be 1.5 for both glaze and varnish.

The glaze+varnish thickness map revealed some brushstrokes with identical width and direction as were seen in the infrared image (Fig. 5b), and other brushstrokes that had more contrast against the rest of the background. The variations in glaze thickness are related to variations in the topography of the black underlayer, and not the brushstrokes Vermeer used to apply the glaze. The thickness measurements are the difference in depth between the relatively flat surface of the varnish+green glaze and the undulating surface of the black underlayer.

The B-scans from the lower right corner show that the underlayer is more corrugated than the painting's surface (Figs. 2g, 3e); therefore it is assumed that the upper surface of the glaze was originally flat due to the 'settling' of the binding medium, which THM-Py-GC/MS analysis determined to be primarily composed of heat-bodied linseed oil. Heating linseed oil to a high temperature (with or without driers) is known to affect its rheological properties: as the paint dries, it 'settles' to form an even, glossy film with few or no visible brushstrokes [22]. The brushstrokes used to apply the glaze are not visible because they levelled out soon after they were applied; this meant that the glaze originally had a relatively flat surface. Now, the overall topography of the painting is dominated by the effects of ageing: cracking, cupped paint, and delamination [23]. This means that it is difficult to extract meaningful quantitative information about the surface of the glaze from MS-OCT.

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**Fig. 5** Mapping of the *Girl*: diagonal line in the upper right marked with a red arrow. **a** Polarised light photograph: René Gerritsen Art & Research Photography. **b** Infrared image (900–1100 nm): René Gerritsen Art & Research Photography. **c** MS-OCT glaze + varnish layer thickness map for the background of the painting. Glazes in the figure could not be detected. **d** MA-XRF map: lead (Pb-M). **e** MA-XRF map: copper (Cu-K). **f** MA-XRF map: potassium (K–K). **g** MA-XRF map: calcium (Ca–K). **h** Detail of the top right corner of **d**, with contrast heightened

### Macroscopic X-ray fluorescence (MA-XRF)

Some of the elements in the glaze were mapped with MA-XRF, which corroborated the elements that were

detected in SEM-EDX mapping of cross-sections (Figs. 2d, 3d, 4c, d). The primary colourants in the glaze—indigo and weld—could not directly be detected using

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**Fig. 6** Detail of upper part of the *Girl*: **a** Infrared image (900–1100 nm): René Gerritsen Art & Research Photography. **b** Photoshop overlay of polarised light photograph (100% opacity) and MA–XRF map for copper (Cu–K) (50% opacity), showing a 'gap' around the edge of the figure

MA-XRF. Indigo usually has no inorganic substrate, and therefore cannot be detected using MA-XRF; however, elements associated with the substrate of weld—calcium (Ca–K, Fig. 5g) and potassium (K–K, Fig. 5f)—can be mapped. Other elements in the glaze mapped with MA-XRF include lead (Pb-M, Fig. 5d) and copper (Cu–K, Fig. 5e). In the background, the quantity of iron (Fe) in the glaze was too low—in comparison to its prevalence in the rest of the composition—to be mapped accurately.

The copper (Cu-K) map in particular shows some interesting features (Fig. 5f). Brushstrokes are visible throughout the background, especially along the upper edge. As determined from the MS-OCT glaze+varnish thickness maps, these brushstrokes are related to the differences in topography of the underlayer, rather than brushstrokes within the glaze. Where the copper intensity is highest (white in the MA-XRF map), the glaze is thicker because the black underlayer (as visualised in the infrared image Fig. 5b) is thinner. The glaze clearly covers the whole background, but stops just short of the contour of the figure (Fig. 6b). There is a gap (appearing darker on the copper map) between the background and the left side of the figure: the front of her jacket, the side of her face and the blue part of the headscarf. This 'gap' is approximately 1–2 mm wide, and in some places a brown underlayer is visible within it; it is a contour that Vermeer intentionally left to soften the transition between the figure and the background [14, 24]. No copper was detected within the figure. This suggests that Vermeer included it in the background glaze to help speed drying, whereas the range of pigments in the figure would have made the paint dry quickly enough without the addition of a copper drier.

#### Variations in the background: a curtain?

In the Mauritshuis 1914 and 1935 catalogues raisonnés, *Girl with a Pearl Earring* was described as having a uniform background with a dark green-brown colour [25, 26]. A remarkable detail on the right side of the background was revealed for the first time during the *Girl in the Spotlight* examination. New information from imaging techniques suggests that it can be interpreted as a curtain.

The MA-XRF maps for the elements found in the glaze—lead, copper, potassium and calcium—show diagonal lines in the upper right and lower right corners of the painting, which resemble folds in fabric (Figs. 5d-g). A detail of the MA-XRF map for lead (Pb-M) shows that Vermeer varied the amount of lead in the glaze to create highlights and shadows (Fig. 5i). The diagonal line indicated by the red arrow is dark in the lead (Pb-M) map because there is a lower lead concentration. Directly next to it is a wider band with more lead; this seems to be a highlight that establishes the modelling of undulating fabric. The Pb-M map shows that the lead is present in the uppermost layer(s), as opposed to the Pb-L map (not shown) which can include lead from deeper in the stratigraphy. Similar 'folds' are visible in the MA-XRF maps for other elements present in the glaze. In the diagonal line indicated by the red arrow, there is a higher concentration of copper, potassium and calcium than the surrounding paint (Fig. 5e-g). The glaze is thicker along this line, as confirmed by the MS-OCT glaze+varnish thickness map (Fig. 5c). This is probably because the underlayer is *thinner* along that line, as indicated by the infrared image (Figs. 5b, 6a) and the glaze spreads out to form an even layer, thus resulting in a thicker glaze + varnish layer, filling in the grooves of the thinner underlayer. Using reflectance imaging spectroscopy (RIS) it was also possible to image the distribution of indigo in the background; variations in the upper right also suggested a folded fabric [27].

Vermeer appears to have established the modelling of the 'curtain' on the right side of the painting at an early stage, during the application of the black underlayer. He further refined the modelling when applying the glaze on top by incorporating some lead-containing pigments. These tonal variations are an original part of Vermeer's concept and were not modified at a later stage. On the left side of the painting, no diagonal lines were detected and the application of the brushstrokes in the underlayer Vandivere et al. Herit Sci (2019) 7:69 Page 14 of 19

are more haphazard. This suggests that the folds of the 'curtain' stop behind the figure of the *Girl*, and that the area to her left was a flat expanse with little modelling.

The diagonal lines that suggest a curtain are barely visible in the polarised light image (Fig. 5a, h) and almost invisible to the naked eye, due to the degradation that has occurred in the background. Especially in the upper right corner, the paint appears blanched and flat, with some areas of shinier, more intensely-coloured glaze. The lower right corner of the background has a slightly warm reddish colour, and above it, one of the 'folds' is barely visible. The degradation that has occurred in the centuries since Vermeer painted *Girl with a Pearl Earring* has changed our perception of the background.

#### Colour, degradation and conservation of the background

To the naked eye, the background of the *Girl with a Pearl Earring* now has an uneven dark tone. After the restoration in 1994, Groen et al. described its appearance as "a dull, milky-grayish green ... washed-out, matte" [2]. They were acutely aware that the visual effect of the background had changed since Vermeer painted it. The colour combination of the yellow lake (weld) and blue dyestuff (indigo) in the glaze indicate that the glaze was originally green. In samples examined in transmitted light, the matrix is yellowish with translucent blue spots (Fig. 2f). Presumably the glaze was semi-translucent when it was first painted, allowing the black underlayer to play a visual role. Other components of the glaze—lead, copper, iron, chalk, gypsum, alum—may have had a minor effect on the colour and translucency of the glaze.

Over the last centuries, the glaze of the background has been affected by light and moisture. Both weld and indigo undergo photo-oxidation when exposed to light, and fade over time [10, 28]. Glazes made with organic lake pigments—especially those containing lakes with a chalk substrate—can become blanched and opaque [29]. The conservation history of the painting and the conditions in which it was kept in the past centuries also had damaging effects. The researchers in the 1990s concluded that it was difficult to connect the current appearance to a particular restoration treatment, but mentioned that those involving water—particularly the aqueous lining in 1881, and consolidation with fish glue—had the potential to cause swelling and contraction, which created microcracks that cause light scattering in the glaze [2, 9].

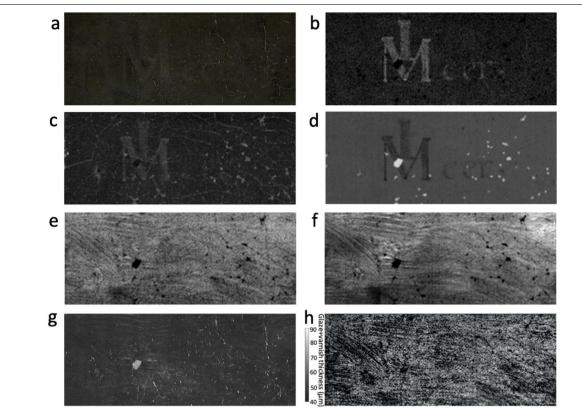
To the naked eye, a small region in the glaze to the left of the *Girl*'s face is better preserved than the rest of the background, so it gives an impression of its original appearance (Fig. 1: white box). While examining the painting under a stereomicroscope during the 1994 restoration treatment, the conservators observed small areas where the background had been masked from the

effects of light and possibly moisture [2, 18]. The areas protected beneath old retouchings and fills appeared darker and more saturated than the surrounding paint. In consultation with the advisory committee that oversaw the restoration, the conservators decided to remove the non-original material, but made no attempt to retouch the darker spots to match the surrounding (degraded) paint, except where the original paint was missing. Nor was it possible or ethically acceptable for the conservators to correct or cover the milky appearance dominating the background.

#### Signature

Vermeer's signature in the upper left corner of Girl with a Pearl Earring has become difficult to see due to the degradation of the background. The letters are barely visible, but they are slightly lighter and warmer in tone than the rest of the background (Figs. 7a, 8a). They read: 'IVM' in ligature, then the letters 'eer'. There is a small damage in the middle of the 'M' that has been filled and retouched. No date could be seen. MA-XRF maps show the signature more clearly than with the naked eye. The elements detected with MA-XRF show that the paint Vermeer used for the signature contains lead white and earth pigments, so it was slightly lighter than the surrounding background. The 'eer' is fainter than the first letters in ligature. In the map for lead (Pb-M) and iron (Fe-K), the signature is brighter than its surroundings, which shows that it contains more lead and iron than the background (Figs. 7b, c).

The position of the signature within the layer structure of the background is difficult to determine with the naked eye, and the information from MA-XRF is inconclusive. In the infrared image, the infraredabsorbing brushstrokes of the black underlayer are not disrupted by the letters, which proves that the letters were painted after the underlayer (Fig. 7g). Where the signature sits in relation to the glaze is more difficult to discern. The evidence from the MA-XRF map for lead (Pb–M) suggests that the signature is situated on top of the glaze. The Pb-M map shows the very superficial part of the layer structure, and as the signature appears light against the dark surrounding background, this implies that the signature is close to the surface (Fig. 7b). The signature in the Ca-K is map is darker than the background, which indicates that it is blocking the signal from calcium (Fig. 7d). The signature is barely visible in the maps for other elements detected in the glaze: potassium (K-K, Fig. 7e) and copper (Cu-K, Fig. 7f). It might be presumed that if the signature were located on top of the glaze, its lead-containing paint would have attenuated the signals for potassium and copper in the glaze layer, especially the potassium signal which is Vandivere et al. Herit Sci (2019) 7:69 Page 15 of 19



**Fig. 7** Signature in upper left: **a** Photograph in polarised light: René Gerritsen Art & Research Photography. **b** MA-XRF map, Pb-M. **c** MA-XRF map, Fe–K. **d** MA-XRF, Ca–K: the white dots are paint losses that were filled with chalk during the 1994 restoration. **e** MA-XRF map, K-K. **f** MA–XRF map, Cu–K. **g** IR photograph: René Gerritsen Art & Research Photography. **h** MS-OCT glaze + varnish thickness map

very low in energy. Alternatively, it is possible that the paint of the signature itself also contains some potassium and copper.

Examination of the same area with MS-OCT is not able to clarify the stratigraphy. The paint of the signature is extremely thin: it cannot be detected in a B-scan or glaze+varnish layer thickness map because the signature is thinner than the thickness variations within the glaze itself (Fig. 7h). It is (barely) visible because the colour and scattering properties of the signature is similar to the background that surrounds it, which MS-OCT cannot detect at this sampling rate.

Images from 3D digital microscopy appears to support the theory that the signature is *on top of* the glaze. The 'IVM' in ligature is faint against the surrounding background (Fig. 8a), and when the image is digitally tilted (beta viewing angle of  $45^{\circ}-50^{\circ}$ ), the topography is dominated by the cracks and the weave of the canvas (Fig. 8b); however, at a higher magnification ( $140\times$ ,  $1.1~\mu m/pixel$ ), the individual pigment particles in the signature are visible. In one of the thin diagonal strokes of the 'M', some white and black particles appear to sit on the surface, *on top of* the glaze; this is somewhat clearer in the tilted 3D

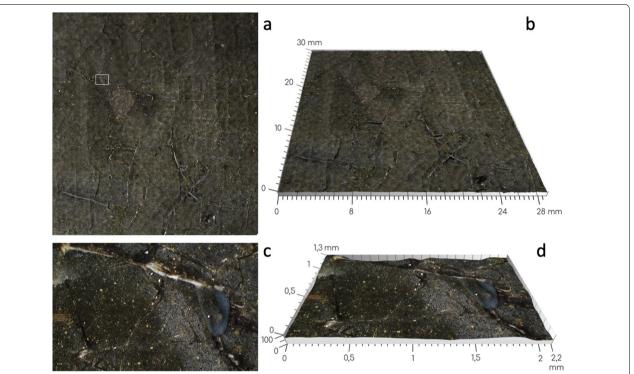
image (Fig. 8c, d). Where cracks are present within the brushstroke of the 'M', the greenish glaze appears to lie beneath.

From the evidence from the non-destructive techniques, we assume the stratigraphy in the area of the signature is as follows: Vermeer applied the black underlayer on top of the ground (Fig. 8c: 1). When this was dry, he applied the glaze (Fig. 8c: 2), then his signature (Fig. 8c: 3). Presumably a sample mounted as a cross-section would clarify the stratigraphy; however, this was not possible as part of this study. Over time, the materials of the glaze throughout the background have degraded, making the signature less visible. Restoration materials—varnish and retouching (Fig. 8c: 4)—were applied during the 1994 treatment [18]. Logically, it would seem that the signature would be one of the last touches that Vermeer applied when he determined that the painting was finished.

# Discussion: Vermeer's working process, and visual effect of the background

The results from the microscopic and macroscopic analyses of the background reveal Vermeer's working process.

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**Fig. 8** a 3D digital microphotograph of the signature. **b** 3D view of **a**, tilted at 45° beta viewing angle. **c** 3D digital microphotograph of area of **a** marked with white box: (1) ground and underlayer in crack, (2) glaze, (3) paint of signature, (4) retouching. Hirox Europe, Jyfel. **d** 3D view of **d**, tilted at 50° beta viewing angle, 1.1 μm/pixel. Hirox Europe, Jyfel

At an early stage in the painting's genesis, Vermeer applied a black underlayer—containing mainly charcoal black, with some minor additions of chalk, gypsum, earth and alum (possibly from a lake pigment)—over the whole area that was to become the background. The addition of a little chalk and gypsum may have improved the handling properties of the black paint. He applied the paint vigorously using overlapping brushstrokes, but somewhat more carefully with wavy horizontal brushstrokes along the top edge (Fig. 6a). Broad forceful brushstrokes were also detected in underlayers in other parts of the painting [15]. The narrow 'gap' that was left between the background and the figure may have softened the contrast between the brightly-lit *Girl* and the dark background.

As charcoal black is a poor drier in oil, Vermeer must have waited some time to allow the underlayer to dry thoroughly before applying the glaze on top. Cross-sections from the background show a distinct separation between the underlayer and the glaze. The greenish glaze, coloured by weld and indigo, would have dried more quickly due to the inclusion of copper, lead and earth pigments. We do not know what kind of brushes he used to apply the glaze, but presumably one was small enough to trace carefully around the contour of the figure; he left a reserve slightly larger than the painted contours of the

figure, creating a 'gap' (Fig. 6b) [11, 15]. The brushstrokes in the glaze are now invisible because the glaze 'settled' soon after it was applied [22].

The glaze layer in the background seems to serve a double function. Firstly, it absorbs scattering reflections originating from the rough black underlayer, which therefore further enhances the darkness of the Girl's background. Secondly, the glaze layer flattens the surface roughness and consequently masks the brushwork of the underlayer. This is an effective method to transform the viewer's perception of a paint surface with brushstrokes into a convincing pictorial illusion of darkness with only specular reflection. A similar strategy to create shadows was found earlier in the oeuvre of Leonardo da Vinci. His enigmatic sfumato technique was studied by Viguerie et al., showing that in the flesh tones, Leonardo used glaze layers with increasing thickness towards the darker areas. Here, too, the function is to both absorb light and to hide the topography of brushstrokes effectively [30].

In his writings, Leonardo advised that if the figure "is both light and dark, put the dark side against a light background and the light side against a dark background" [31, 32]. Perhaps this is the effect that Vermeer was attempting to create by juxtaposing the *Girl*'s back (in shadow)

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against the lighter part of the background, and the left (lit) side of the *Girl* against the darker, unmodulated background. The background of *Girl with a Pearl Earring* stands in sharp contrast with the figure. In the lightest parts, the figure is not only very reflective, but also was more thickly painted with some *impasto*: notably, the white paint used in the *Girl's* collar [23]. Vermeer therefore maximises the contrast between the *Girl* and the background by using a number of opposing optical paint properties, both at and below the paint surface. He applied a dark, absorbing, translucent glaze with flat topography in the background, whereas the figure is light, very reflective and contains some impasto.

This pronounced contrast contributes greatly to the dramatic lighting in the painting. The Girl is brightly lit against what would have originally been an extremely dark background, creating the impression of a person who suddenly and spontaneously turns towards the viewer from total darkness. There is, however, little to no detail on the left side of the background itself. In photographic terms, its dynamic range is very low. Whereas the human eye has a great dynamic range and is almost instantly able to adapt to changing lighting conditions, photographic projection reduces the dynamic range in images significantly. Dark appears darker, light appears lighter and the number of greyscales in between is reduced. It is exactly this photographic effect, we hypothesise, that Vermeer attempted to create in the Girl with a Pearl Earring. We know that lens technology was available around that time [33]. Could Vermeer have been inspired by the image with low dynamic range that a camera obscura would have produced?

Opposed to the homogenously flat backdrop on the left side of the Girl, the 2018 discovery of diagonal lines in the upper right corner suggests the presence of a dark green curtain. A similar compositional device in the background of Vermeer's Mistress and Maid (c. 1667, Frick Collection, New York) was recently researched at The Metropolitan Museum of Art, New York [34]. Examination using infrared reflectography found that Vermeer originally painted a tapestry in the background of Mistress and Maid, and later modified it to depict a curtain. The curtain was originally "translucent dark green. Its current faint brown color is the result of the pigments having darkened over time. Pigment degradation also accounts, in part, for the relative loss of depth and form of the curtain" [34]. Although no earlier composition was found in the background of Girl with a Pearl Earring, it is interesting to note that Iacono comments on similarities between the two paintings and remarks: "Unlike [the background] in the Girl, the background in Mistress and Maid includes remnants of a drawn curtain."

Other paintings from Vermeer's oeuvre that feature green curtains include: Girl Reading a Letter at an Open Window (c. 1659, Gemäldegalerie Alte Meister, Dresden) and Woman Writing a Letter with her Maid (c. 1670, National Gallery of Ireland, Dublin). Vermeer painted ornate tapestries that are restricted to only one side or corner of the composition in: The Art of Painting (c. 1666–1668, Kunsthistorisches Museum, Vienna), The Love Letter (c. 1669, Rijksmuseum, Amsterdam), and Allegory of the Catholic Faith (c. 1670–1672, The Metropolitan Museum of Art, New York). In these examples, however, the figures are placed in the space behind the curtain, rather than in front of it.

#### **Conclusions**

The combination of micro- and macroscale examination techniques used during the 2018 *Girl in the Spotlight* examination analysed the composition and distribution of the layers that Vermeer used to paint the background in a more in-depth way than was possible in the 1968 and 1998 studies [1, 2].

Microscopic samples re-examined with SEM-EDX and FIB-STEM determined that the black underlayer contains primarily charcoal black, and no bone black as was suggested during the previous research in 1994 [2]. These techniques also identified the inorganic materials present in the glaze, including the presence of a copper drier. LC analysis of the glaze confirmed the colourants that had been found in 1998: weld and indigo. THM-Py-GC/MS found that the binding medium is primarily composed of linseed oil, slightly heat-bodied.

Complementary imaging techniques mapped the distribution of the underlayer and glaze. MS-OCT plotted the distribution of the glaze+varnish, and showed that the differences in thickness were related to the roughness of the brushstrokes in the underlayer. Groen et al. [2] concluded that the glaze was originally an "even, smooth, glossy, translucent, hard green paint, made to look darker and given depth by a dark underpaint." The recent research shows that while the glaze appears to be even in colour on the left side, Vermeer intentionally mixed a little lead white into the glaze to vary the colour on the right side. Furthermore, Vermeer had already conceived of this modelling early in the painting's genesis, as the infrared images showed that he also varied the thickness of the black underlayer in these areas. Rather than a flat backdrop, the diagonal 'folds' in the background suggest a draped fabric—possibly a curtain—that puts the *Girl* into a defined space but still draws our focus to her brightlylit face and clothing.

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#### Abbreviations

DTMS: direct temperature-resolved mass spectrometry; ESA: emission spectrographic analysis; FIB–STEM: focused ion beam–scanning transmission electron microscopy; FTIR: Fourier transform infrared spectroscopy; FTIR-ATR: Fourier transform infrared spectroscopy—attenuated total reflectance spectroscopy; HPLC: high performance liquid chromatography; LC: liquid chromatography; MA-XRF: macroscopic X-ray fluorescence; MA-XRPD: macroscopic X-ray powder diffraction; MS-OCT: multi-scale optical coherence tomography; Py-TMAH-GC/MS: pyrolysis-tetramethylammonium hydroxide-gas chromatography mass spectrometry; RIS: reflectance imaging spectroscopy; SEM-EDX: scanning electron microscopy—energy dispersive X-ray analysis; UHPLC-PDA-FLR: ultra-high-performance liquid chromatography with a photodiode array, attached to a fluorescence detector; THM-Py-GC/MS: thermally assisted hydrolysis and methylation, pyrolysis gas chromatography—mass spectrometry; UV: ultraviolet.

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#### Authors' contributions

AV wrote the main body of the text and was the Head Researcher for the Girl in the Spotlight project. AvL performed light microscopy and SEM-EDX analysis at the Ateliergebouw, Amsterdam. AvL also did the MA-XRF examination, interpretation of the SEM-EDX, FIB-STEM, and MA-XRF results, and contributed to the content of the text. TC performed the MS-OCT examination, provided images and interpretation of the results, and reviewed the relevant parts of this publication. RH carried out the SEM-EDX mapping and FIB-STEM analyses at Shell Technology Centre Amsterdam (STCA) and reviewed and contributed to the relevant parts of this publication. ANPG performed the UHPLC-PDA-FLR analysis at the Cultural Heritage Agency of the Netherlands, provided information about historical indigo sources, and reviewed the relevant parts of the text. HvK performed the THM-Py-GC/MS analysis at the Cultural Heritage Agency of the Netherlands, and reviewed the relevant parts of the text. EL carried out the examination with the Hirox 3D digital microscope, provided the relevant images, and wrote the section with the experimental method. JD wrote the section in the discussion about the dynamic range of the painting, and interpreted some results of MS-OCT and MA-XRF. All authors read and approved the final manuscript.

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#### Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request. The datasets supporting the conclusions of this article are included within the article and its additional files.

#### **Competing interests**

The authors declare that they have no competing interests.

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