

Investigation of Materials Used by Edvard Munch

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*The pigments and paint binders used by Edvard Munch have been investigated in several studies. Munch used a mixture of media in his works of art. The two versions of *The Scream* studied here were found to include oil paints and oil paints thickened with beeswax and also oil crayons containing beeswax and Japan wax, as well as casein pastels, a paraffin wax crayon and at least one gum-bound paint. His sketches on canvas make use of oil paints and tempera paints including egg and casein, as well as casein pastels in at least one instance. His oil paintings on canvas seem to have been executed using a more conventional technique, with most having one or a few paint layers bound with linseed oil on a ground formed from lead white in oil on top of a ground made of chalk in glue. Munch's palette is not extensive, though he was reasonably willing to introduce new materials, such as his use of a petroleum-based wax crayon in 1893, oil pastel – possibly as early as 1893 and certainly by 1910, and his use of cadmium red by 1927–1929. The identification of materials has informed conservators who are planning and carrying out conservation treatments.*

INTRODUCTION

In spite of the importance of Edvard Munch and the notorious complexities of his painting technique, there have been few publications regarding the materials used by this artist. Kuckova et al. employed enzymatic cleavage and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy to identify animal glue as the binder in the grounds, and egg tempera as the paint binder, in samples from Edvard Munch's paintings *Separation* and *Portrait of Friedrich Nietzsche* dated 1893 and 1905, respectively [1]. Table 1 indicates all the pigments, binders and extenders reported by these authors. The same group of workers concluded that whole egg was used as the binder in a sample from *Sitting Nude and Grotesque Masque* dated 1893 [2]. Frøysaker described the 'Aula project', which is concerned with the conservation of paintings of Edvard Munch which hang in the Assembly hall of Oslo University (the 'Aula') [3]. She reports on the conservation and preliminary identification of drying oil

as the binder in a number of paint samples, through the use of Fourier transform infra-red (FTIR) microscopy [3, 4]. Frøysaker and Liu subsequently carried out an extensive investigation of *Chemistry, New Rays, Women Harvesting* and *The Fountain* using in situ X-ray fluorescence (XRF) to analyse elements in the pigments and hence to make suggestions for the pigments present [5]. Literature results (Table 1) suggest the use of different grounds, containing lead white and chalk or zinc white, and in the paint layers at least 18 different pigments have been suggested. Frøysaker also reports that many colours were made from complex mixtures. It has been mentioned that Unn Plahter also previously examined both versions of *The Scream*; first in 1974 and subsequently in 1992 [6]. She tested the yellow pigment in the two versions of *The Scream* and another painting from 1906 and found cadmium yellow. Some differences between the pigments used in the earlier version of *The Scream* and the two other paintings were demonstrated and the results are soon to be published [7].

The National Museum in Denmark has previously carried out some analysis of a sketch for *Alma Mater/The Researchers* (Museum inventory number M 1091).

Received ?

Table 1 *Painting materials reported in the literature as a result of previous analysis of Munch's painting*

Painting, date	Author and reference	Identification of materials found [1], [2] or suggested [5]
<i>Separation</i> , 1893	Kuckova et al. [1]	Animal glue binder in ground, egg tempera in paint. Vermilion, zinc white, cadmium yellow and Emerald green ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$) as the pigments. Aluminium phosphate and kutnohorite ($\text{Ca}(\text{Mn}, \text{Mg})(\text{CO}_3)_2$) as extenders and some metallic brass
<i>Portrait of Friedrich Nietzsche</i> , 1905	Kuckova et al. [1]	Animal glue binder in ground, egg tempera in paint
<i>Sitting Nude and Grotesque Masque</i> , 1893	Kuckova et al. [2]	Egg tempera binder in paint
<i>Chemistry</i> , 1909–1916	Frøysaker and Liu [5]	Cadmium yellow, chrome yellow, a copper green, a chrome green, Emerald or Scheele's green, cerulean blue, ultramarine blue, Prussian blue, cobalt blue, vermilion, organic red, cobalt violet (cobalt phosphate), zinc white, as pigments; zinc white, lead white and chalk in the ground
<i>New Rays</i> , 1909–1916	Frøysaker and Liu [5]	Cadmium yellow, chrome yellow, strontium chromate, a chrome green, a copper pigment, ultramarine blue, cobalt blue, vermilion, organic red, cobalt pigment, manganese violet, organic black, lead white, zinc white as pigments; zinc white, lead white and chrome yellow in an under-paint; zinc white, lead white and chalk in the ground
<i>Women harvesting</i> , 1909–1916	Frøysaker and Liu [5]	Cadmium yellow, a copper green, cerulean blue, ultramarine blue, Prussian blue, cobalt blue, vermilion, organic red, red ochre, cobalt violet?, manganese violet, zinc white, lead white as pigments; zinc white, lead white and chalk in the ground
<i>The Fountain</i> , 1909–1916	Frøysaker and Liu [5]	Cadmium yellow, chrome yellow, a copper pigment, Emerald or Scheele's green, green earth, cerulean blue, ultramarine blue, cobalt blue, vermilion, organic red, red ochre, manganese violet, zinc white as pigments; zinc white, lead white and chalk in the ground

According to their reports, the work was painted with pigments that had been mixed with boiled linseed oil, and some possibly also with poppy seed oil, on a white, water-sensitive ground that contains very little binding agent. There is a surface coating which was applied as a consolidant in 1951 and which was shown to be gelatine [8]. The sketch examined in Denmark is a different work from the two sketches on this subject matter reported upon here.

Part of the work mentioned here regarding *The Sick Child* was previously published in a museum catalogue [9] and is referenced accordingly where this is so. Some of the present authors also previously described an analysis of the binder in white paint from *Towards the Light*, which was demonstrated to be linseed oil with animal glue in the ground [10]. In the report of a method for the analysis of yellow flavonoid pigments, one example given is the analysis of the organic pigment component of one of the yellow paints taken from *The Scream* 1893, which is a buckthorn berry 'lake' [11].

In this paper, materials from a number of works of art by Edvard Munch spanning the period 1885–1927 are investigated. The works include oil paintings, works of mixed media on cardboard, and sketches of mixed media on canvas. The research questions concern the extent of

the range of materials used by Munch and, in particular, a comparison of the materials and techniques used in the two versions of *The Scream*. We were also interested to see whether Munch adopted new artists materials as they became available during his lifetime. Knowledge of the materials present in Munch's works may also be useful to conservators when planning conservation treatments. This knowledge may also enhance our understanding of the poor condition of some of the works and the water sensitivity of some of the paints. For example, data on the multilayered structure in *The Sick Child* [12], the range of binders used in both versions of *The Scream* [13–17], and the fragility of the paint in *The Human Mountain: Towards the Light* [18] have been recognized as useful knowledge for the planning of a safe and effective conservation strategy to treat and preserve these paintings. *The Scream* (1910?) and *Madonna* (1894) were stolen from the Munch Museum in 2004 [19]. When the paintings were returned in 2006, it was obvious that they had suffered damage. Examinations were conducted in order to assess the nature and extent of this damage. Research was resumed with an emphasis on the preservation aspects of the paintings, as well as on the question of their specific material and technical traits, adding valuable information to the previously published material [13–17, 19].

ANALYTICAL STRATEGIES

Pigment analysis was carried out with polarized light microscopy (PLM) using a scheme of optical tests based on those suggested by McCrone [20], Wülfert [21] and Easthaugh et al. [22], in combination with energy dispersive X-ray (EDX) elemental analysis and, where appropriate, with FTIR spectroscopy. Either staining tests using Ponceau S and Sudan Black B stains on cross-sections of paint, or FTIR spectroscopy on paint fragments, gave an initial indication of the type of binder present. Subsequently, binder analysis was complemented with an appropriate method using derivatization and gas chromatography–mass spectrometry (GC-MS). A transesterification/methylation method was employed to derivatize oil-based binders, resins or waxes [23]. Oils were recognized by their palmitate/stearate ratios and the degree of heat bodying estimated from their ratios of dicarboxylic acids [24, 25]. The occurrence of methyl esters of dehydroabiatic acid ((1R,4aS,10aR)-1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-phenanthrene-1-carboxylic acid) and 7-oxodehydroabiatic acid ((1R,4aS,10aR)-1,4a-dimethyl-9-oxo-7-(1-methylethyl)-3,4,10,10a-tetrahydro-2H-phenanthrene-1-carboxylic acid) were considered as indicators of coniferous resin, probably pine resin [26]. A series of straight-chained alkanes

(paraffins) ranging from C₂₆ (hexacosane) to C₃₃ (trtriacontane) with a peak at C₂₉ (nonacosane), with even- and odd-numbered carbon atoms having equal importance, indicates a fossil wax such as paraffin wax or ceresine [27]. In contrast, a series of alkanes ranging from C₂₆ to C₃₃ with a peak at C₂₇ (heptacosane), with odd-numbered carbon atoms predominating, together with a range of carboxylic acids of higher molecular mass than stearic acid, showing a peak at tetracosanoic acid, were taken to indicate beeswax [27]. Japan wax is indicated by the presence of certain dicarboxylic acids, and this is discussed below. Amino acid analysis, combined with analysis of fatty acids as their propyl esters [10], was employed for proteins or protein/oil mixtures, and hydrolysis followed by silylation allowed sugar and uronic acid analysis for suspected gums [28, 29].

INVESTIGATION OF TWO EARLY OIL PAINTINGS ON CANVAS

Edvard Munch, The Sick Child 1885/86 (reworked 1896), National Museum of Art, Architecture and Design, Oslo

An oil painting, *The Sick Child* (NG.M.00839) (Figure 1), showed many layers, supporting the hypothesis that it had been reworked several times [30]. *The Sick Child* is considered to be Edvard Munch's breakthrough painting and was first exhibited in Kristiania (now Oslo) in 1886. Munch, in his writings, has described how he fought with the image for a year: painted, wiped out, repainted, scraped off, etc. until it was 'heavy as lead'. His statement is confirmed by early photographs and X-radiographs, and we know that the composition and execution did not find its final form until around 1896 [30]. The painting has an original varnish, with some of Munch's own retouching on top [12]. The analyses, carried out currently, have helped in understanding Munch's process of painting and in differentiating between several phases of execution.

Many of the cross-sections analysed show the same multilayered structure as can be seen in the section made from sample 1 (Figure 2) from the blue/grey area on the top left of the painting (Figure 1) [9]. With so many layers, it is not surprising that microscopic examination and EDX analysis showed the presence of several different pigments, as summarized in Table 2. For example, copper and arsenic were found both in the green-blue layer at the top of the sample of the blue/grey paint at upper left (sample 1) and in the green particle in the lower layers, probably indicating the



Figure 1 Edvard Munch, *The Sick Child* 1885/86, 1896, showing sample sites.

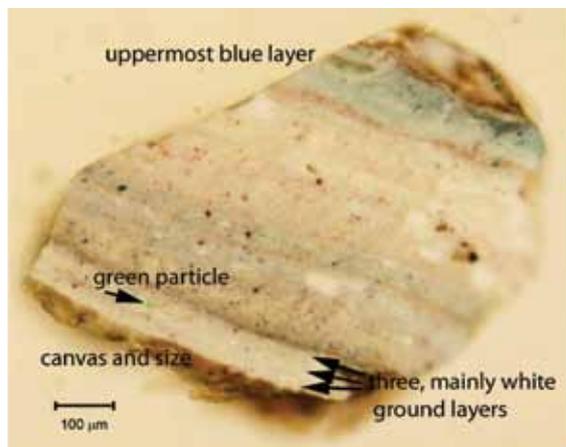


Figure 2 Cross-section of sample 1 from Edvard Munch, *The Sick Child* 1885/86, 1896.

presence of emerald green (Schweinfurt Green) [31], a pigment found previously in works by Munch (Table 1) [1, 5]. Many of the pigments previously found by Frøysaker in later works (Table 1) were also discovered in *The Sick Child*, with the addition of bone black and umber (Table 2) [5, 9]. While Kuckova had found egg tempera paint in some of his early works (Table 1) [1, 2], the present study reveals that Munch used linseed oil and pine resin in the ground and linseed oil in the paint in *The Sick Child*. Beeswax is also present, seemingly in

the paint layer, but this finding should be treated with caution since beeswax was also found in a previous lining from 1954 and some of this material was also used to consolidate the front of the painting in places [12]. It is possible that the pine resin found in the ground could also have penetrated from the wax/resin lining.

Edvard Munch, Madonna 1894, Munch Museum

In contrast to *The Sick Child*, the layer structure in *Madonna* (oil on canvas, 90 × 68.5 cm) (Figure 3) is much simpler [19, 32] with generally only one or two, often translucent, paint layers on two ground layers. As an exception to this, the red halo around the woman's head is substantial and is applied covering other layers. Alongside the application of paint with brushes there is also paint applied by spraying, since small droplets of colour can be traced over almost the entire surface. In some areas the paint is scratched by the artist. This can be seen along the right side of the torso, locally in the face, and on the left shoulder and hair. Currently, the painting's surface has a non-original varnish.

A typical structure can be seen in sample 7 from the greenish blue paint on the right (Figure 4). Staining with Ponceau S indicated a protein binder in the lower ground on this and other cross-sections from the same work. Subsequent staining with Sudan Black indicated an oil binder in the upper ground and paint layers in all the cross-sections from this work. Several of the paints

Table 2 Materials identified in paint samples from *The Sick Child* 1885/86 (reworked 1896) as previously reported [9]

Sample number	Colour, description	Identification of materials found
1	Paint layers from blue/grey area upper left	Drying oil, possibly walnut or poppy seed oil, pine resin, beeswax, lead white, zinc white, ultramarine blue, vermilion, an organic red lake on an alumina base, red ochre, possibly umber, Emerald green or Scheele's green, barites and an unidentified chromium pigment
2	Paint layers from green area, lower right edge under tacking margin	A drying oil, pine resin, beeswax, lead white, zinc white, ultramarine blue, charcoal, bone black, red ochre, yellow ochre, possibly umber, emerald green Scheele's green, and a chromate, possibly lead chromate
3	Paint layers from pink area, upper tacking margin, to right of centre	Linseed oil, pine resin, beeswax, lead white, zinc white, ultramarine blue, vermilion, red ochre, cadmium yellow, cobalt blue and a chromate, possibly lead chromate or zinc yellow
4	Paint layers from red area on moulding of chest of drawers, left edge	Drying oil, possibly walnut or poppy seed oil, pine resin, beeswax, lead white, zinc white, ultramarine blue, vermilion, red ochre, yellow ochre, umber, Emerald green or Scheele's green, barites, possibly talc and a chromate, possibly lead chromate
5	Paint fragment from 'over-paint' on damaged area, bottom right	Drying oil, possibly walnut or poppy seed oil, pine resin, beeswax, cobalt blue, vermilion
6	Paint fragment from edge of damage close to over-paint, bottom right	Drying oil, ultramarine blue, vermilion, lead white, chalk

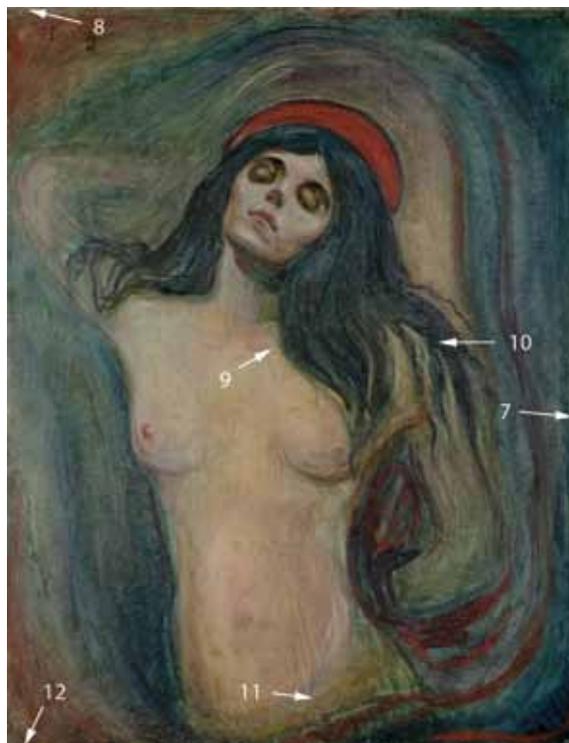


Figure 3 Edvard Munch, *Madonna* 1894, showing sample sites.

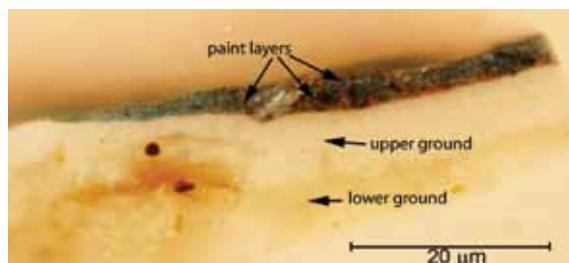


Figure 4 Cross-section of sample 7 from Edvard Munch, *Madonna* 1894.

were separated from the ground and analysed with GC-MS (Table 3). The binders in the paints were shown to be heat bodied linseed oil, with the inclusion of beeswax in the case of the greenish blue paint, sample 7, and possibly some poppy oil or walnut oil in the case of the blue paint in the hair, sample 10. A sample of exposed ground at bottom left (upper white ground, sample 12), was also confirmed with GC-MS to contain linseed oil mixed with small quantities of coniferous resin, probably pine resin.

There seems to be a similar range of pigments in *Madonna* (Table 3) to those found in *The Sick Child* except that while a copper pigment is indicated, no arsenic could be found to suggest the presence of either Emerald green or Scheele's green (copper hydrogen arsenite) and thus the precise identity of this pigment cannot be specified [31]; furthermore, no umber was found in *Madonna*. Such 'Copper greens' were also reported in later works by Frøysaker [5].

Interestingly, in the chromatogram obtained for the paint layer from the dark blue paint in the hair of the figure (sample 10), in addition to peaks related to the binding media, a small peak was also found for 1,8-dimethoxyanthraquinone, dimethyl ether (danthron, dimethyl ether). This was probably derived, during the methylation process, from danthron or its glycoside, which is found in several plant sources including *Aloe* species and also frangula bark (*Rhamnus frangula*) [33]. Hence a possible explanation is that this paint contains either a yellow lake pigment prepared from frangula bark or the material known as 'aloes' which was derived from certain *Aloe* species, including *Aloe vera*, and was sometimes used in painting as a yellow glaze [34].

The general conservation strategy for *Madonna*, together with previous visual observation and technical examination, has been reported [19], but its detailed conservation treatment has yet to be published. The current analysis of this painting provides new data and broadens our understanding of the work of art as a physical object.

A COMPARISON OF TWO VERSIONS OF THE SCREAM

Edvard Munch, *The Scream* 1893, *The National Museum of Art, Architecture and design, Oslo*

The Scream (tempera and oil on unprimed cardboard, 91 × 73.5 × 0.35 cm), the epitome of expressionist art painted in 1893 by Edvard Munch, has – despite its fame and high cultural and art historical importance – never before had a thorough scientific examination of its materials and their application. This painting is now in a state of advanced degradation, particularly the wavy lines in the sky applied with coloured pastels or crayons [17]. Here, the binder has migrated to the surface, creating a crust that flakes off to expose the powdery pigments (Figure 5), and the present identification of these materials will be important for the understanding of this process and to the planning of the conservation of the painting.

Table 3 Materials identified in paint samples investigated, from Madonna 1894

Sample number	Colour, description	Identification of materials found
7	Blue (greenish), right side, on top of two white ground layers	Zinc white, charcoal, Prussian blue, ultramarine blue, vermilion, chalk and lead chromate in heat bodied linseed oil with beeswax Grounds as in sample 12
8	Brown (reddish), top left, on top of two white ground layers	Zinc white, lead white, vermilion, a brownish red sienna or ochre and yellow ochre in oil Grounds as in sample 12
9	Flesh colour, upper torso (pink over the flesh colour is sprayed painting) on top of two white ground layers	The paint layer contained zinc white, a trace of lead white, vermilion, and yellow ochre. Binder: Heat bodied linseed oil
10	Dark blue hair on figure, on top of two white ground layers	The paint layer contained zinc white, a trace of lead white, Prussian blue, ultramarine blue lead chromate, and vermilion with an unidentified copper based pigment and possibly some aloes or yellow lake based on frangula bark. The binder is a heat-bodied linseed oil possibly with a little poppy oil (or walnut nut oil)
11	Green (brownish) lower part of figure, on top of two white ground layers	The paint layer contained zinc white, chalk, a trace of lead white, charcoal, and yellow ochre in an oil binder
12	Ground, exposed at bottom left edge. Sample consisting just of ground	Two layers of ground present Upper ground: lead white in linseed oil and pine resin Lower ground: chalk in animal glue

**Figure 5** Detail of crust on pink crayon from *The Scream* 1893, site of sample 24.

The Scream (Figure 6) is executed on cardboard, with no ground, and contains mostly single layers of oil paints, oil/tempera emulsions and several types of crayon and pastel (Table 4). The crust on the pink crayon from the upper left (sample 24) (Figure 5) was found to contain mainly ceresin or paraffin wax (Figure 7) with coniferous resin and, in addition, some source of palmitic and stearic acids, perhaps stearin wax. These materials seem to have diffused from the crayon and have formed a crusty bloom. The materials found are reported as being used, in the late nineteenth century, to make

'grease pencils' [35], the forerunner of the non-toxic paraffin wax crayons famously created for the education market in 1903 by Binney and Smith [35]. Interestingly, a scarlet red crayon produced by Binney and Smith is said to have been present among Munch's paints held in the Munch Museum, though this would have been produced a little later than the date of this painting [36]. At present, the Munch Museum has in its possession 925 tubes of paint from his studio but currently no crayons. The paints are being investigated.

Binder analysis on the red paint in the sky at the upper left (sample 18) indicated an oil paint thickened with beeswax. Another oil-wax mixture was discovered in the orange finish, or 'secondary' touch in the upper right portion of the sky (sample 15). This sample, when analysed with GC-MS, lacked the usual pattern of hydrocarbons and had a different pattern of carboxylic acids than that found in beeswax. Most interestingly, C₂₀ and C₂₂ dicarboxylic acids (eicosanedioic and docosanedioic acids, as their methyl esters), indicative of Japan wax, were found (Figure 8) and a reference sample of Japan wax (Cornelissen, London) gave a similar chromatogram. Japan wax [26, 37], is a vegetable tallow derived from *Rhus* (sumac) berries and is used in pencils, oil pastels and crayons [35, 38, 39]. Japan wax contains a large amount of glycerol tripalmitate, which prevents the identification of the drying oil. Thus the binder present in sample 15 is probably a mixture containing Japan wax and a drying oil, possibly demonstrating an



Figure 6 Edvard Munch, *The Scream* 1893 recto (left) and verso (right), showing sample sites.

early use of oil-based pastel. 'Oil crayons' or 'paint sticks' are reported to have been invented by J.F. Raffaelli, who gave as one recipe: 'Madder lac, 160 grammes, linseed oil 200 grammes, virgin wax (beeswax) 50 grammes, and Japanese vegetable wax (Japan wax) 50 grammes' [40]. Raffaelli used these crayons in work exhibited in 1902, so possibly similar materials may have been available to Munch for a few years before this date. Also, amongst the contents of Munch's studio materials J.F. Raffaelli oil crayons and two of Gunther Wagner's oil crayons have been reported [36].

The range of pigments present in the various media used (Table 4) contains many of those used in the oil paints discussed before; but here, cadmium yellow (cadmium sulphide) was identified in some of the yellow samples investigated: in the oil-bound paint found in the yellow highlight on the hand rail at lower right (sample 13); in the oil/casein paint found in the warmer yellow brushstroke which runs under it (sample 14); in sample 28 from the yellow rail; and also in sample 36 from the yellow on the verso. Interestingly, the infrared spectra of these yellows indicated the presence of barium sulphate, for example in sample 13. Barium

sulphate was seen by microscopy to be present as barites but not intimately mixed with the cadmium sulphide as it would be in lithopone. Also, EDX analysis of a yellow particle in sample 13 indicated the presence of cadmium and sulphur and a little zinc, as expected, but not barium [41]. This indicates that the cadmium yellow used is cadmium sulphide, which was commercially available from 1846, and not cadmium yellow lithopone (cadmium sulphide with barium sulphate) which was not patented until 1921 and introduced into the fine art market a few years later [41, 42].

The blue to the right of the main figure (sample 20) contains ultramarine. For conservation purposes we were concerned with the water sensitivity of this paint. GC-MS analysis showed that the largest proportion of the binder in this sample is gum Arabic, though protein analysis also showed the presence of a mixture which may contain a little animal glue as well as casein and egg. Hence this blue may be water-colour paint, modified with other binders.

Two surface deposits were also analysed, both appearing as grey splashes of matter having fallen at a sharp angle from above. The grey splashes to the right of the

Table 4 *Materials identified in paint samples investigated, from The Scream 1893*

Sample number	Colour, description	Main pigments and binder found
13	Yellow, lower right – finishing, 'secondary' touch (upon no. 14). Contains (probably) some red from vertical paint at far right	Cadmium yellow (CdS) and barium sulphate Linseed oil
14	Yellow, lower right (under no. 13 and slightly warmer)	Cadmium yellow and barium sulphate, vermilion, charcoal, an organic yellow containing rhamnetin, probably a buckthorn berry lake (previously reported [11]) Casein/drying oil emulsion possibly some egg also present
15	Orange, Upper right - finishing, "secondary" touch	Lead chromate, gypsum Drying oil with Japan wax, possibly an oil pastel
16	Red upper right, may contain bluish red from vertical paint at far right	Vermilion and gypsum Drying oil with egg mixture with trace of animal glue (probably the paper size)
17	Red, upper left (similar to sample 16)	Vermilion and gypsum Oil/protein mixture
18	Red upper left cooler than 16 - finishing, 'secondary' touch	Vermilion and gypsum Drying oil with beeswax, possibly an oil pastel
19	Turquoise, upper left	Viridian (chromium oxide dihydrate), lead white, lead chromate Linseed oil with beeswax
20	Blue (dark) to the right of main figure (dissolves easily in water)	Artificial ultramarine blue, barites, clay, zinc white, mainly gum Arabic with casein, egg and a drying oil, elemental sulphur
21	Red from vertical paint at far right - finishing, 'secondary' touch	Vermilion, red lake on a gypsum base? Linseed oil and coniferous resin
22	Green at right - finishing, 'secondary' touch	Viridian Drying oil with beeswax, possibly an oil pastel
23	White 'crayon', upper left	Lead white and charcoal Casein and fats (possibly milk fats) (possibly some egg) probably a casein pastel
24	Pink 'crayon', crust, upper left	Lead white and vermilion Wax crayon containing mainly ceresin or paraffin wax with some source of palmitic and stearic acids, possibly stearin wax (or possibly some bloom as free acids or metal soaps from an underlying oil containing layer). Also contains coniferous resin
25	White dirty and oily, upper left	Lead white, zinc white and barites Casein and linseed oil (possibly some egg), possibly a casein pastel
26	Blue 'crayon', to the right of the man in the top hat	Ultramarine blue and gypsum Casein and fats, possibly milk (possibly some egg), probably a casein pastel
27	Green, 'crayon' to right of main figure	Viridian, clay, zinc yellow (potassium zinc chromate, $KZn_2[CrO_4]_2(OH)$), Prussian blue Casein (possibly milk) and egg mixture, probably a casein pastel
28	Yellow from rail	Cadmium yellow
29	Brown, from rail, lower right	Ultramarine blue, charcoal and an iron oxide red
30	White, highlight from rail	Lead white, zinc white and ultramarine blue
31	Brown from last signature	Red ochre and red lake on an alumina base
32	Paper support, hot water extract	Gelatine or animal glue size
33	Reverse side, red upper left	Vermilion
34	Reverse side, blue, upper left	Ultramarine blue, lead white, barites Casein and linseed oil with trace of animal glue (probably the paper size)
35	Reverse side, white upper left	Lead white, zinc white
36	Reverse side, yellow, at right	Cadmium yellow Protein

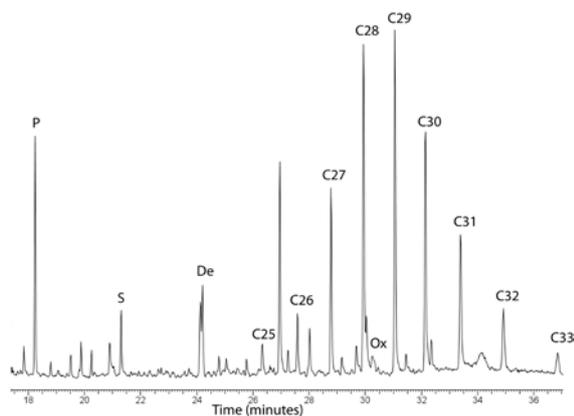


Figure 7 Chromatogram (17–37 minutes) of methyl esters and alkanes derived from sample 24, pink crayon crust: C25 = pentacosane, C26 = hexacosane, C27 = heptacosane, C28 = octacosane, C29 = nonacosane, C30 = triacontane, C31 = untriacontane, C32 = dotriacontane, C33 = trtriacontane, identified as paraffin wax; De = methyl dehydroabietate, Ox = methyl 7-oxodehydroabietate, identifying the presence of a coniferous resin; P = methyl palmitate, S = methyl stearate, indicating fat, non-drying oil or stearin wax.

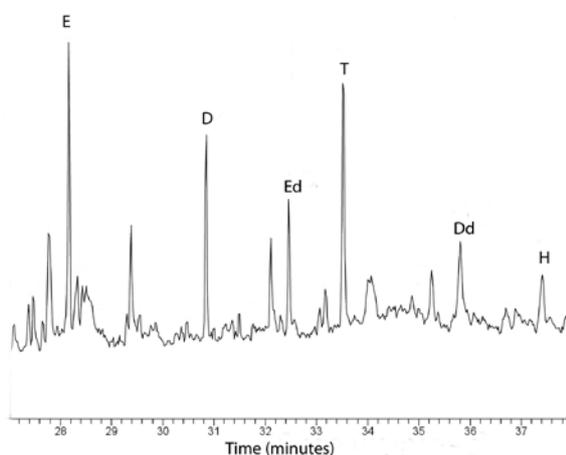


Figure 8 Chromatogram of methyl esters derived from sample 15; E = methyl eicosanoate, D = methyl docosanoate, Ed = dimethyl eicosandioate, T = methyl tetracosanoate, Dd = dimethyl docosandioate, H = methylhexacosanoate.

figure around the rails, were found by GC-MS to be tallow, perhaps from a candle. On the other hand, the grey splash of material on the edge of the arm on the left of the figure where it meets the middle rail, showed a peak for sulphates or phosphates at 1100 cm^{-1} as well as typical amide bands at 1640 and 1540 cm^{-1} in the infra-

red spectrum, appearing similar to a reference spectrum of bird excrement. Elemental analysis revealed that the deposit contains mainly carbon with magnesium, aluminium, silicon, phosphorus, sulphur, potassium, calcium and zinc, which were also the elements found in our reference sample of bird excrement. The finding of bird excrement may relate to the fact that Munch left many of his paintings outdoors, allegedly to be weathered. 'My pictures seem to need a bit of sunshine, some dirt, and a little rain to bring about the colour harmony,' one of his biographers reports [43].

Both findings indicate that the painting has never been cleaned, not even when it was in private hands before being given to The National Gallery in 1910. Thus, its worn and soiled state should probably be considered as part of the artistic process, severely challenging future treatments [44]. The whole range of binders present, from water-sensitive gum to paraffin wax, will also have to be taken into account in planning any conservation.

The Scream 1910(?), Munch Museum

This version of *The Scream* (tempera and oil on unprimed cardboard, $83.5 \times 66\text{ cm}$) is neither signed nor dated (Figure 9). Recent research has established that the painting probably stems from around 1910 [6, 7, 13]. It is executed on pressed cardboard [13, 15–17]. As with the earlier version, there is no ground and the cardboard is visible on the surface of the painting where parts are not covered by paint. The paint layer thickness varies from quite thin to impasto areas, characteristic for most of the reds in the sky. The paint is applied both diluted and not diluted. Although paint is predominant for this version of the motif, there are other materials used as well; for example, the head and neck are drawn with both green and yellow crayons. The work is not varnished.

Cross-sections made from the paints indicated some multiple layering, more common here than in the earlier version, caused by painting one feature on top of another. For example, the brownish red from the upright post to the right of the figure (sample 40) is painted over an orange paint from the rail and a blue and yellow mixture from the background (Figure 10). Other cross-sections, for example the orange and pale blue paints in sample 37 from the rail (Figure 11) indicate wet-in-wet mixing.

It is shown here that the media include paints with oil binders and tempera paints or pastels containing casein and egg (Table 5). There are also yellow, orange and pink lines in the sky that seem in character and appearance to

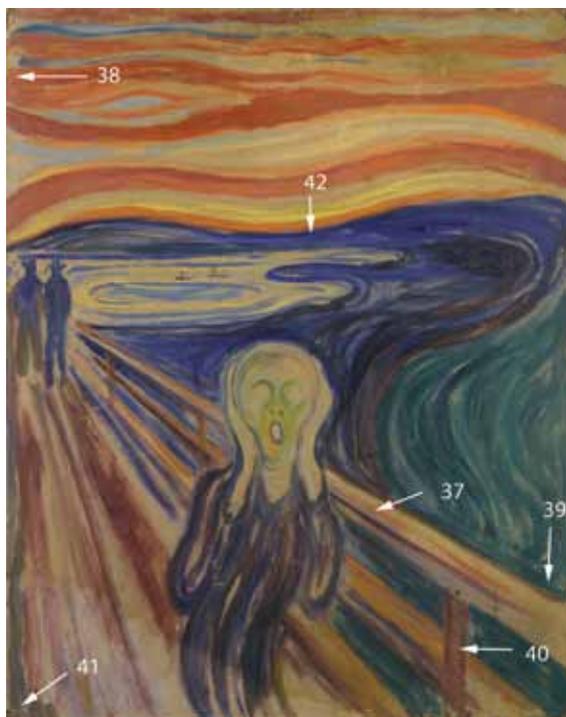


Figure 9 Edvard Munch, *The Scream* 1910(?) showing sample sites.

be oil pastel and, indeed, the orange layer in sample 38 from the sky contained oil and beeswax and is probably an oil pastel, which were certainly available by 1910 [40]. As in the previous version, the finding of mixed media has necessitated careful planning of the conservation protocol.

The 1910(?) version of *The Scream* (Table 5) contains many pigments found in the earlier version, including

cadmium yellow, vermillion, viridian (hydrated chromium (III) oxide), ultramarine blue, a red lake and zinc white, and in this version cobalt violet (cobalt phosphate) has also been employed. Cobalt phosphate is a pigment also found in the *Aula* paintings [5], painted from 1909 to 1916, and so it may be possible to say that Munch introduced this pigment to his works around 1909/10. No ochre or lead white was found, despite the finding of these pigments in the previous version.

INVESTIGATION OF FIVE SKETCHES ON CANVAS

A number of sketches on canvas from the Munch Museum in Oslo have also been investigated: *The History*, 1910/11; *Women Harvesting*, 1910/11; *New Beams*, 1910/13; *Alma Mater/The Researchers* (museum number M 965), 1910/11; and 'Alma Mater, right-hand section' (M 961), 1912/13. Edvard Munch painted these five sketches as studies for the final paintings for the University of Oslo's *Aula*, as studied by Frøysaker [3–5]. Materials from the sketches were investigated as part of the preliminary documentation for the Munch Museum's project 'Paintings stored on rollers'. This project encompasses 47 previously un-stretched sketches on linen and cotton canvases. Munch painted 32 of these 47 sketches for the University of Oslo's *Aula*, eight for *The Human Mountain: Towards the Light*, and three for the decoration of the City Hall in Oslo. The remaining four sketches are of other motifs. 43 of them have never been examined before, but during the project they will be thoroughly documented, examined, analysed and treated. In fact the five examples reported here are representative of a more extensive programme of analyses of pigments, binders and efflorescence which has so far been carried out on 29 of the sketches and which will be published more fully in the future. All the samples reported here

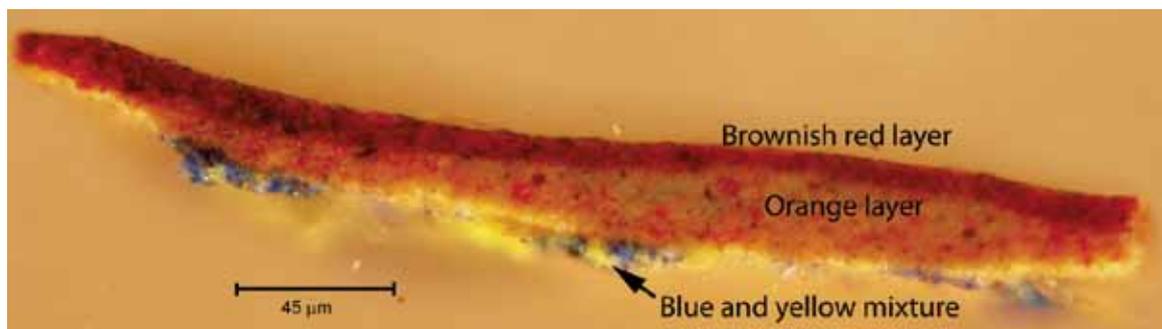


Figure 10 Cross-section of sample 40 from the brownish red paint on the post, showing the layer structure.

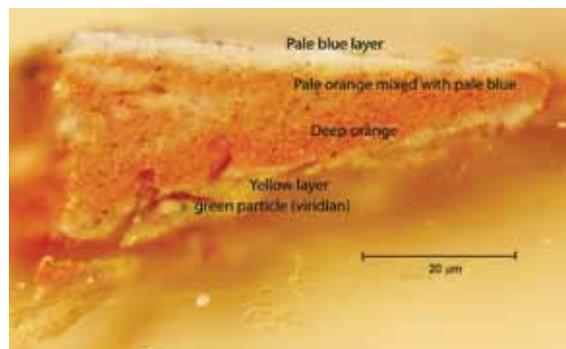


Figure 11 Cross-section of sample 37 from the rail, showing the blending of paint layers.

have been taken from areas with single-layer structures. In fact many of the paints in these five sketches consist of only single layers, with one or several mixed pigments.

Binders were investigated via combined oil and protein analysis. A linseed oil binder was found in the blue paint sample on the vest of the central bearded figure and one of the white samples of the sky in the upper right quadrant, which were taken from *The History* and also in a sample of the thin and matte green

paint from the grass to the right of the figures taken from *Women Harvesting*. On the other hand, protein-based binders were found in the red from the trousers of the bearded figure and white paints at the right edge of the figures taken from *The History*, and also in the upper yellow/white paint from *New Beams* (specifically some casein and egg were found here) (Table 6). Small amounts of glue seem to be mixed in with the proteinaceous binder.

The present authors investigated a thin and matte white paint layer from the sky at top left on a sketch for *Alma Mater/The Researchers* (M965) and found by FTIR analysis that it contained aragonite, with a very small amount of calcite (two polymorphs of calcium carbonate), and is thus probably shell white (Table 7). The small amount of binder present was shown by GC-MS to be raw linseed oil. The white paint from the central blue and white area in another sketch for the 'right-hand side of *Alma Mater*' (M961), on cotton canvas contained lead white, zinc white and chalk, and both linseed oil and animal glue binders. Interestingly, a white efflorescence was present on the left of the head of the figure, which was shown by FTIR analysis to be basic zinc carbonate (zinc carbonate hydroxide) $Zn_5(OH)_6(CO_3)_2$ (Table 7) [45, 46].

Table 5 Materials identified in paint samples investigated, from *The Scream 1910(?)*

Sample number	Colour, description	Identification of materials found
37	Pale blue over pale orange over a deeper orange layer over a yellow layer (possibly crayon?) From the rail to right of figure	Pale blue layer contains mainly zinc white with a little ultramarine blue, vermilion and cadmium yellow in a casein/egg binder Pale orange layer contains zinc white, vermilion and cadmium sulphide Deeper orange layer contains mainly vermilion and a little zinc white, in a mixture of a drying oil and beeswax. This may be an oil pastel Yellow layer contains mainly cadmium sulphide with vermilion, zinc white and viridian in casein /egg binder
38	Red and orange layers from sky, top left	Mostly vermilion and some red lead, with a trace of chalk, a little Prussian blue and charcoal. The binder seems to be a mixture of oil and beeswax
39	Green to right of rail	Mostly viridian with some ultramarine blue, vermilion and zinc white in dark green. More zinc white and also cadmium yellow as well as viridian and vermilion in the paler green layer. Binder is a drying oil, possibly a linseed oil/poppy seed oil mixture, with a trace of pine resin
40	Brownish red from upright post to right of figure, brownish red layer over orange over a yellow. Cadmium yellow and ultramarine blue in the lowest layer and a trace of viridian, layer containing a mixture of blue and yellow pigments	Red lake on an alumina base and vermilion with zinc white, chalk, and some cadmium yellow and ultramarine blue in the lowest layer and a trace of viridian, Casein and egg are the main binders present
41	Thin violet layer over red layer from brown and violet mixed area bottom left	Red paint has mostly red lake on an alumina base with cadmium yellow and vermilion and a brownish-yellow lake possibly based on frangula bark. The violet layer contains cobalt violet (phosphate type), vermilion, cadmium yellow and zinc white. Binder is a drying oil, possibly poppy seed oil with a trace of pine resin
42	Pink layer over red layers from red sky over figure where red meets the blue area	Red lake on an alumina base, and also zinc white, and vermilion. Some viridian. Some layers may contain casein, others linseed oil

Table 6 Materials identified in paint samples investigated, from three sketches by Munch: a sketch for *The History 1910/11*, sketch for *Women Harvesting 1910/11*, and sketch for *New Beams (New Rays) 1910/13*

Sample number and sketch	Colour, description	Identification of materials found
43 <i>The History</i> M960	Blue, thick matte and opaque paint layer, left edge of figures	Ultramarine blue with very little linseed oil binder
44 <i>The History</i> M960	Red, thick semi gloss paint layer, centre, on trousers	Casein binder, trace of animal glue, from size?
45 <i>The History</i> M960	White, right edge of figures	Chalk, protein binder, seems to be a mixture of animal glue and egg
46 <i>The History</i> M960	White, right edge	Chalk and linseed oil
47 <i>The History</i> M960	Unknown, adhesive-like material (size?) from trousers	Animal glue
48 <i>Women Harvesting</i> M 915	Green, thin matte and opaque paint layer, grass to right of figures	Linseed oil, pigment not investigated
49 <i>New Beams</i> M918	Yellow/white, thick matte and opaque paint layer, upper part, left of centre	Protein binder, mainly casein and a trace of animal glue

Table 7 Materials identified in paint samples investigated from two sketches for *Alma Mater/The Researchers*

Sample number and sketch	Colour, description	Identification of materials found
50 Sketch for <i>Alma Mater/The Researchers</i> M 965	White paint, a thin matte and opaque layer from sky, top left	Very little raw linseed oil binder and shell white
51 Sketch for <i>Alma Mater</i> , right-hand section M 961	White paint from central blue and white area	Animal glue and linseed oil both present. Pigments include zinc white, lead white and chalk
52 Sketch for <i>Alma Mater</i> , right-hand section M 961	White efflorescence from left of head of figure	Zinc hydroxide carbonate

The samples analysed in these five sketches are taken from very porous paint layers. This porosity is an unfortunate property of several paints in all these 47 sketches. One explanation offered by the analysis is that the binders are minor components of the paints, as has been found in another sketch [8]. The fragility of some of the paints may also be explained by the fact that the zinc oxide pigment is reacting with the environment, forming a zinc carbonate hydroxide efflorescence. The ongoing analysis will contribute to further conservation research on Munch's sketches and paintings, particularly in the period from 1909 to the late 1920s.

INVESTIGATION OF A LATER PAINTING ON CANVAS

The Human Mountain: Towards the Light, 1927/29, Munch Museum

The large painting *The Human Mountain: Towards the Light* (oil on canvas, 300 × 420 cm) is unvarnished, which is typical of Munch's work [44, 47]. The paint

layer thickness varies from thin, sometimes even translucent, to thick, with areas of local impasto. During 2006 the painting was examined and treated. The painting is an extensively fragmented image with much exposed canvas, a condition visible on photographs taken during Munch's lifetime. A major challenge for the conservation is the extent of flaking paint, which was observed on all areas of the canvas [18].

The painting has two ground layers [18]: analysis showed that the lowest is a chalk ground in animal glue, and the upper ground contains lead white in heat bodied linseed oil (Table 8), just as in the much earlier *Madonna*. Some of the paints are single layers on the two grounds, such as the white, yellow, green and red paints, while other samples showed a more complex structure, with two or three layers such as the blue, greyish white and violet paints (Table 8).

Some extenders such as silica (silicon dioxide) are present in this work, which are different from the ones that have been documented so far. Some different pigments were also found here: the red paint from the

Table 8 Materials identified in paint samples investigated from *The Human Mountain: Towards the Light 1927/29*

Sample number	Colour, description	Identification of materials found
53	White, top layer of paint, upper edge	Lead white with some silica extender (in heat-bodied linseed oil as previously reported [8]), on top of the two grounds
54	Upper ground, upper edge	Lead white in heat bodied linseed oil
55	Lower ground, upper edge	Chalk ground (in animal glue as previously reported [10])
56	Yellow, top left corner, near edge, single paint layer on two grounds	Cadmium yellow mixed with a trace of lead white and clay in heat-bodied linseed oil
57	Red, top left corner, near edge, single paint layer on two grounds	Cadmium red mixed with a little red lake on an alumina base and some lead white in a heat-bodied linseed oil
58	Blue, left edge, has blue and green paint layers	Blue layer, containing ultramarine blue and a small amount of viridian, or possibly chromium oxide green. Beneath this is a green layer containing ultramarine blue and both viridian and cobalt blue, or perhaps the rarer cobalt chromium aluminium oxide, and a trace of lead chromate or lead white. The binder for these paint layers appears to be a heat-bodied linseed oil
59	Green, bottom right, single paint layer on two grounds	Viridian, cobalt blue, lead white, silica, clay and cadmium red in heat-bodied linseed oil
60	Violet, top left corner, has a violet layer on blue on another violet layer	The top violet layer contains a mixture of pigments including cobalt violet light (cobalt arsenate), lead white, clays and zinc white. The blue layer contains cobalt blue and lead white and zinc white. The second violet layer contains cobalt violet light (cobalt arsenate), lead white, silica and zinc white. The binder for these paint layers was identified as heat-bodied linseed oil
61	Greyish white, from sky area, near 'mountain' of people, has a greyish white containing some blue particles on another white layer on the two grounds	The two white layers contain a mixture of poppy seed oil and linseed oil

top left (sample 57) contains cadmium red (cadmium seleno-sulphide) mixed with a little red lake on an alumina base and some lead white. Cadmium red was patented in 1892 but was not commercially available until 1910 [42]. The absence of barium in the EDX analysis showed that the cadmium red is pure cadmium seleno-sulphide and not cadmium red lithopone, which also contains barium sulphate and was introduced in 1926, shortly before this work was finished [42]. In the violet paint the two violet layers contain a mixture of pigments (Table 8) including cobalt violet light (cobalt arsenate) as confirmed by microscopy and the finding of cobalt and arsenic by EDX analysis. The yellow brushstroke from the top left (sample 56), contains cadmium yellow mixed with a trace of lead white and clay. As in the yellows from *The Scream*, the cadmium yellow here is pure cadmium sulphide, and not cadmium yellow lithopone.

The small patch of blue on the left side has mainly ultramarine in the uppermost blue layer, but EDX analysis showed the presence of chromium, which suggests a small amount of viridian, or possibly

chromium oxide green (chromium (III) oxide). The presence of chromium and cobalt in the green layer below may indicate both viridian and cobalt blue, or perhaps the rarer cobalt chromium aluminium oxide. Lead is also present, which may indicate a trace of chrome yellow or lead white.

As Frøysaker discovered in other works [5], some paints in this work contain a complex mixture of pigments, for instance, the green from the bottom right includes viridian, cobalt blue, lead white, silica, clay and cadmium red.

The binder for most of the above paint layers was shown by GC-MS analysis to be a heat-bodied linseed oil. However, the greyish white paint from the sky area, near the 'mountain' of people, has two layers of white paint which both have higher palmitate/stearate ratios (2.77 and 2.60) than the other paints, suggesting a mixture of poppy seed oil and linseed oil [24, 48]. Such mixtures are often used in tube paints containing white pigments and other pale colours, since poppy seed oil has a paler colour and less of a tendency to yellow than linseed oil [49]. Walnut oil is also a possibility, but this oil

was more commonly used in early Italian paintings [24] and not in early twentieth-century Northern European paintings, where the mixture of poppy seed oil and linseed oil is a more likely explanation for the palmitate/stearate ratio found. Poppy seed oil has a greater tendency to crack than linseed oil and hence this may explain the greater degree of degradation in this area of the painting [49].

CONCLUSIONS

In this extensive technical study of several works illustrating various periods in Munch's oeuvre it was found that the artist used a mixture of media in his works of art on cardboard and also in his sketches on cotton canvas. In the two versions of *The Scream*, oil paints and oil paints thickened with beeswax were used, as well as casein pastels, wax crayon, oil pastels containing beeswax and Japan wax, and at least one gum-bound paint. His sketches on canvas are executed with oil paints and tempera paints including egg and casein-bound paints, as well as, in at least one instance, casein pastels and, in another, the use of oil pastel (Table 9).

Two oil paintings on canvas examined here seem to have been executed using more conventional techniques, having one or only a few paint layers bound with linseed oil, or in one case a poppy seed and linseed oil mixture. These paintings have an upper ground formed from lead white in oil on top of a lower ground composed of chalk in glue. However, one early painting that was examined (*The Sick Child*) had many layers of paint, indicating many stages of reworking.

This study found 22 different pigments and six different extenders or pigments usually associated with grounds; hence it could be said that Munch's palette was not extensive (Table 9). Some of the materials found are reported to have been present among the contents of the artist's studio conserved at the Munch Museum [36]. Many of the pigments found were also identified by other authors in the Aula works [5]. It seems that Munch was reasonably willing to introduce new materials as they became available, as illustrated by his use of a petroleum-based wax crayon in 1893, soon after their introduction, his use of oil pastel (oil crayon) perhaps as early as 1893 and his use of cadmium red by 1927/29.

The analysis revealed various reasons for fragile or flaking paint and water sensitivity in some of the works and has influenced the planning of conservation treatments, especially where a variety of binders have been found within the same object or where ethical issues have been raised.

EXPERIMENTAL DETAILS

Polarized light microscopy (PLM)

Samples of the pigments were treated with dichloromethane to soften any oil present and crushed between glass slides to separate the pigment particles, then mounted on microscope slides with Meltmount 1.66 resin and examined with a James Swift MP3500A polarizing microscope using methodology developed by McCrone and modified by others [20, 21, 22].

Scanning electron microscopy

Small flakes of each of the samples to be analysed were either mounted on carbon pads on aluminium stubs or mounted in cross-sections prepared from fast-setting acrylic resins. Images and elemental analysis of each sample were achieved by EDX analysis using a FEI XL30 environmental scanning electron microscope, fitted with a Rotec analyser.

Chemical spot test for ultramarine

A small amount of sample was treated with 40 µl of concentrated hydrochloric acid. The hydrogen sulphide gas evolved was identified by smell, and any colour change was noted.

Fourier transform infra-red (FTIR) analysis

A sample of each paint or adhesive/coating was placed onto the diamond window of a Durascope diamond ATR attachment linked to a Perkin Elmer 1000 FTIR spectrometer. Each sample was pressed down against the window using a metal anvil and scanned 16 times. The background scan was automatically subtracted. The sample was thus analysed by reflectance FTIR.

Staining tests for binders on cross-sections

In order to look for protein binders, cross-sections were stained with either acid fuchsin (1% in water) or Coomassie Blue (1% in water) depending on the colour of the paint layer. The stains were left on the section for 20 minutes and then rinsed several times with water.

To look for the presence of oil binders, cross-sections were stained with Sudan Black B (1% in 70% aqueous ethanol). The stain was left on the section for 20 minutes and then rinsed several times in 50% aqueous ethanol.

Table 9 Summary of findings

Title and Date, Museum, description	Pigments and extenders found	Binders found	Grounds Adhesives and other assorted materials found
<i>The Sick Child</i> 1885/86 / reworked 1896 Nasjonal Musseet for Kunst, Arkitektur og Design, Oslo Oil on canvas	Zinc white, lead white, artificial ultramarine blue, cobalt blue, vermilion, an organic red lake on an alumina base, red ochre, umber, Emerald green (or possibly Scheele's green) yellow ochre, cadmium yellow, a chromate possibly chrome yellow, charcoal, bone black. Barites, chalk and possibly talc	Linseed oil, linseed mixed with poppy oil (or possibly walnut)	Pine resin and beeswax from a later lining adhesive Pine resin and linseed oil in a varnish layer
<i>Madonna</i> 1893-94 Munch Museum, Oslo Oil on canvas	Zinc white, lead white, Prussian blue, ultramarine blue, vermilion, red ochre, chrome yellow (lead chromate), yellow ochre, charcoal, unidentified copper-based pigment, aloes or frangula bark lake, chalk	Heat-bodied linseed oil, a mixture of linseed and poppy oil, mixture of linseed oil and beeswax	Upper ground: lead white in linseed oil and pine resin Lower ground: chalk in animal glue
<i>The Scream</i> 1893 Nasjonal Musseet for Kunst, Arkitektur og Design Mixed media on paper	Cadmium yellow (cadmium sulphide), vermilion, viridian, chrome yellow, charcoal, lead white, zinc yellow (potassium zinc chromate), Prussian blue, ultramarine blue, red ochre, red lake on an alumina base, buckthorn berry lake. Barium sulphate, gypsum, china clay	Paraffin wax or ceresine wax crayon, casein pastels, oil paint, possible oil crayons consisting of drying oil with beeswax and drying oil with Japan wax, casein/oil emulsions, egg/oil mixture, protein/gum Arabic mixture	Gelatine paper size, bird excrement, tallow or similar animal fat surface deposit
<i>The Scream</i> 1910(?) Munch Museum Mixed media on paper	Zinc white, cadmium yellow (cadmium sulphide), red lead, cobalt violet dark (cobalt phosphate), organic brown lake (possibly based on frangula bark), viridian, Prussian blue, ultramarine blue, red ochre, red lake on an alumina base	Proteinaceous tempera paints, or possibly pastels which seem to be casein /egg mixtures and casein/ egg/glue mixtures Also some oil paints including linseed oil and poppyseed oil/pine resin drying oil with beeswax, mixtures, at least one of which is an oil pastel	–
<i>The History</i> 1910/11 Munch Museum Mixed media sketch on canvas	Ultramarine blue, chalk	Casein, egg, linseed oil	Animal glue size or adhesive
<i>Women Harvesting</i> 1910/11 Munch Museum Oil (or mixed media) sketch on canvas	–	Linseed oil	–
<i>New Beams</i> 1910/13 Munch Museum Casein pastel sketch on canvas	–	Casein	–
Sketch for <i>Alma Mater / The Researchers</i>	–	–	Shell white in raw linseed oil ground
Sketch for <i>Alma Mater</i>	–	–	Zinc white, lead white and chalk in linseed oil with animal glue in ground Basic zinc carbonate efflorescence
<i>The Human Mountain: Towards the Light</i> 1927 Munch Museum Oil on canvas?	Lead white, zinc white, cadmium yellow, cadmium red, ultramarine blue, viridian, cobalt blue, cobalt violet light (cobalt arsenate)	Heat bodied linseed oil binder in paints The white paints contain a linseed oil/poppyseed oil mixture	Heat-bodied linseed oil binder in upper ground Animal glue in lower ground

Protein and oil analysis via GC-MS

Samples were transferred to a Reacti-Vial™ and were hydrolysed with concentrated hydrochloric acid (40 µl) at 9°C for 3 days. The acid was removed under vacuum and the residue treated with propan-1-ol/ dry hydrogen chloride mixture (80 µl) at 110°C for 45 minutes. The excess reagent was evaporated under nitrogen at 50°C and the residue was dissolved in 5% pyridine in dichloromethane (80 µl). Pentafluoropropionic anhydride (80 µl) was added and the mixture was heated to 100°C for 15 minutes. The excess reagent was evaporated under nitrogen at room temperature and the residue was dissolved in dichloromethane (80 µl). This procedure [10] yielded the propyl esters of the N-pentafluoropropanoyl derivatives of the amino acids in the proteins and also propyl esters of the fatty acids released by hydrolysis of any drying oil present, which were then analysed by GC-MS. The GC-MS instrument used was a Thermo Focus GC fitted with a DSQ mass detector. Typically the column used was a Thermo TR-5 15 m column and the temperature of the column was raised from 35°C to 290°C within the run.

GC-MS analysis of oils, resins and waxes

Each sample was transferred to a Reacti-Vial™ and was derivatized and subjected to chromatographic analysis by gas chromatography and mass spectrometry (GC-MS). The sample was heated with 5% methanolic solution of 3-rifluoromethylphenyltrimethylammonium hydroxide (120 µl) to 60°C for 5 hours [23]. Toluene (80 µl) was added to the mixture in order to help dissolve any hydrocarbons present [50]. The mixture was then subjected to thermal decomposition at 250°C in the injection port, before analysis by GC-MS in order to look for evidence of drying oils, waxes and resins in the paint. The GC-MS instrument used was a Thermo Focus fitted with a DSQ mass detector. Typically the column used was a Thermo TR-5 15 m column and the temperature of the column was raised from 60°C to 290°C within the run.

GC-MS analysis of gums

The sample was transferred to a Reacti-Vial™ and was derivatized and subjected to chromatographic analysis by gas chromatography and mass spectrometry (GC-MS) via the published method [28, 29]. The sample was heated with concentrated aqueous trifluoroacetic acid (TFA) (80 µl) to 105°C for 0.5 hours. The TFA

was then evaporated from the sample. Pyridine (Aristar) (80 µl) was added to the mixture in order to dissolve any sugars present. Further TFA (80 µl) was added followed by hexamethyldisilazane (HMDS) (120 µl). The mixture was then shaken at 25°C for 1 hour, before analysis by GC-MS in order to look for evidence of sugars and uronic acids derived from any gum present. The GC-MS instrument used was a Thermo Focus fitted with a DSQ mass detector. Typically the column used was a Thermo TR-5 15 m column and the temperature of the column was raised from 60°C to 290°C within the run. A total ion count was made but the chromatogram was clarified by looking at the peaks given by selected ions, mass; 191, 204 and 217.

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