

Anselm Kiefer: a study of his artistic materials

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Abstract The style of the contemporary German artist Anselm Kiefer is highly innovative and unconventional and is characterized by the use of diverse materials that he selects and combines according to the emotions that they stir in him. The conservation and preservation of works by Kiefer are particularly difficult tasks because of the heterogeneity and, in some cases, the incompatibility of the materials used; therefore, a thorough characterization is crucial before any intervention is considered. In this paper, we report the results of an investigation on a fragment from a multimaterial work and on samples from the paintings *Bohemia Lies by the Sea* and *Die GröÙe Fracht*. The large fragment was cut by the artist himself from a work in progress and is considered destitute of any artistic value; therefore, it was possible to sample it extensively. This fragment and the samples from the *Die GröÙe Fracht* and *Bohemia Lies by the Sea* paintings were analyzed by ultraviolet (UV) fluorescence imaging, fiber optic reflectance spectroscopy, Fourier transform infrared spectroscopy, nuclear magnetic resonance, Raman spectroscopy, X-ray

diffraction, gas chromatography-mass spectrometry, and pyrolysis gas chromatography-mass spectrometry. This multitechnique approach allowed us to fully characterize and identify pigments, dyes, and organic components that reflect the diversity of the materials typically chosen by the artist. The results are evaluated in the context of the interview that Antonio Rava had with the Anselm Kiefer in 2000.

Keywords Anselm Kiefer · Contemporary art · Noninvasive spectroscopy · Conservation

1. Introduction

Anselm Kiefer was born in 1945 in Donaueschingen and received his training in the second half of the 1960s under the guidance of Joseph Beuys. In 1969, he had his first exhibition at the Kunstverein in Hanover. Already in the early 1980s, he was considered one of the greatest exponents of German contemporary art. Today, his curriculum is that of a famous master who has exhibited in the most important museums and galleries of the world.

Kiefer has been appreciated mostly out of Germany where, initially, he was associated with the neo-Nazi movement by several art critics because of his provocative actions. As reported in the literature (Albano 1998), he photographed himself with the *heil* salute in front of some historical German buildings. He later explained that it had been an intuitive and mechanical act dictated only by irony. Kiefer has tried to interpret the aesthetics of the Nazi years with the will of redeeming German history and freeing it from the shadows of the past. Unfortunately, many people have not comprehended his artworks' real meaning, and for a very long time, Kiefer suffered from being called a Nazi. Due to this misunderstanding, he moved from Germany to Barjac, in southern France, in

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1992. Since then, the countryside of Provence has been the primary source of inspiration for a new creative phase that set the look on his vision of the fragile human condition that he compares with the power of nature.

Kiefer's style, highly innovative and unconventional, is characterized by his use of very diverse materials that he selects and combines according to the emotions that they stir in him. To quote the artist: "I only use materials that speak to me. [...] I don't believe that the Idea can be found everywhere—the Idea in the sense of spirit is already present in the material. For example, lead: it's the material of melancholy, of black rancor. Once, in an old house, I saw a lead drainpipe and that material—lead—literally fascinated me" (Rumma et al. 2006). In most of his works, Kiefer employed lead, in its solid form or dropped after melting, alone or in combination with other materials (Cacciari and Celant 1997; Eccher 1999; Celant 2008).

The artist has also made particular use of photographs, vegetable items (e.g., straw, dried plants or flowers, and burnt wood), ash, sand, volcanic earths, and iron wire. He has used materials picked up from the land around his studio or collected from around the world. He created an archive of plants and flowers from which restorers have to draw in case they have to replace components in his works. However, he is not concerned about the aging of his artworks because he intends them as dynamic objects aimed to inspire different feelings and interpretations in future viewers.

His enormous production has included permanent installations, sculptures, as well as paintings on canvas and wood, usually characterized by large dimensions. Kiefer's preferred painting materials has involved the use of an emulsion of oil colors in a cellulose paste, which he has produced in his *atelier*. The emulsion is applied in thick layers on a support and left to dry for at least 1 year. In this way, the surface acquires the cracked appearance typical of his paintings and "becomes the ideal foundation for the application of color which, on the whole, is painted on with the idea of glazing rather than the application of a consistent substance" (Chiantore and Rava 2005, 2013).

The transportation, installation, and conservation of Kiefer's artworks are problematic because of their large size, heterogeneity, and in some cases, the incompatibility of the materials used. The risk of degradation is high due to the possible detachment of the components, organic matter decomposing or coming under biological attack, and the nature of the support that can easily suffer deformation (Lindner et al. 2004; Griffin et al. 2014). To address, and possibly minimize, these problems it is necessary to characterize and identify these components, their compatibility and their modes of deterioration.

In the frame of the Italian project Preventive Conservation of Contemporary Art (COPAC, PAR-FAS Tuscan Region, 2011–2013), funded by the Region of Tuscany, a number of

Kiefer's artworks were selected in order to study the materials and their application to help conservators and curators in the difficult task of preserving the artefacts. The first object investigated was a large fragment (approximately 18 cm×300 cm) of painted canvas that was given by Anselm Kiefer to Antonio Rava during an interview (Chiantore and Rava 2005 and 2013) in 2000 in Barjac, in southern France, where the artist worked at the time, during which it was possible to visit his studio and storage, and to thoroughly discuss his technique. The artist himself cut this large fragment (Fig. 1), called "the strip" in the text, from a finished painting executed in Barjac, in 1996–1997, in order to reduce its size for exhibition. Kiefer gave away the strip for research purposes only and expressly refused to authorize its display since for him it has lost all artistic status. The strip was analyzed by noninvasive techniques, and five samples were also removed for further investigation.

The second work included in our study is *Bohemia Lies by the Sea* (MMA 1997.4a, b, Fig. 2), a large-scale landscape on burlap (191.1 cm×561.3 cm) in the collection of The Metropolitan Museum of Art in New York dating from 1996, when the artist was working in Barjac. This composition is characteristic of Kiefer's command of scale and his combining deep perspective with exceptionally rich impastoed surfaces, his robust and sculptural paint application, as well as his dramatic color contrast, all resulting in an imposing presence.

This work is painted on two distinct panels, each 191.1 cm×280.7 cm, joined together along the center of the composition. The media include oil, emulsion, shellac, charcoal, and powered paint on burlap. A small fragment of the paint layer, which was found to have spontaneously detached from the surface while the artwork was on view, was saved as a sample. This sample was analyzed for the present study.

A third work, *Die Größe Fracht*, exhibited on the South wall of the main reading room in the San Giorgio library in Pistoia, was also investigated (Fig. 3). This large paint on canvas (460 cm×690 cm), finished in 2007, perfectly

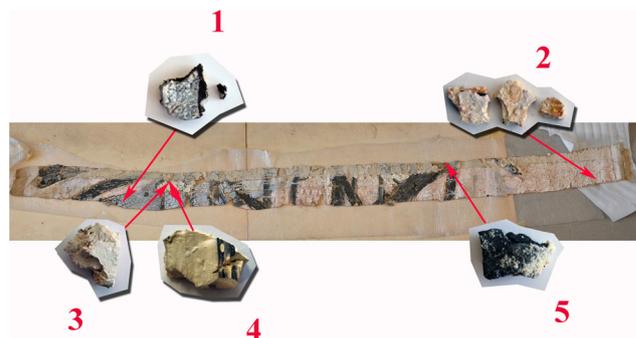


Fig. 1 Paint fragment named 'the strip' (18 cm×300 cm), a study piece donated by the artist to Antonio Rava. The locations where samples for analysis were removed from are indicated. The description of each sample is reported in Table 1

represents the pictorial concept of the artist (Calabrese and Corà 2007). Notwithstanding its young age, this work was subjected to a partial restoration by Antonio Rava in 2011 due to the detachment of paint from the canvas support. Four samples from this artwork were analyzed.

The following combination of techniques was used for materials characterization: fiber optic reflectance spectroscopy (FORS), ultraviolet (UV) fluorescence imaging, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, proton nuclear magnetic resonance (^1H NMR), X-ray diffraction (XRD), gas chromatography-mass spectrometry (GC/MS), and pyrolysis gas chromatography-mass spectrometry (Py-GC/MS).

2. Materials and methods

Sample description

The samples from the different works analyzed are listed and described in Table 1. Sampling positions are reported in Figs. 1 and 3 for the strip and *Die GröÙe Fracht*. The exact location of the sample from *Bohemia Lies by the Sea* is unfortunately impossible to precisely identify due to the fact that it was found on the gallery floor below the painting. However, it is reasonable to assume that it came from the bottom edge of the painting, which has shown vulnerability in the past.

Fiber optic reflectance spectroscopy

FORS was applied in the ultraviolet–visible–near-infrared (UV–Vis–NIR) spectral range (350–2,200 nm) using two Zeiss spectrum analyzers: models MCS 601 UV–Vis and MCS 611 NIR 2,2 WR, and a 20 W halogen lamp source (mod. CLH600) mounted on a single chassis. To investigate the 270–800 nm (UV–Vis) range, we used a Zeiss spectrum analyzer model CLX 500 equipped with a Xenon lamp. With



Fig. 2 *Bohemia lies by the Sea* (191.1×561.3 cm, 1996) by Anselm Kiefer. The Metropolitan Museum of Art (1997.4a, b). Purchase, Lila Acheson Wallace Gift and Joseph H. Hazen Foundation Purchase Fund,

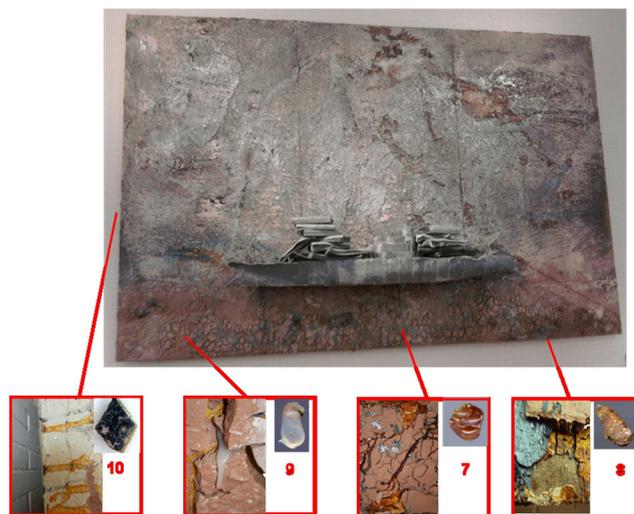


Fig. 3 Overall view of *Die GröÙe Fracht* (460×690 cm, 2007) in the San Giorgio library in Pistoia, indicating the locations where the samples for analysis were taken from

both instruments, a probe-head with an 8°/8° geometry was employed (Bacci et al. 2009).

Fourier transform infrared spectroscopy

FTIR spectra in the transmission mode were recorded using two different devices: a Nicolet Protégé® 460 E.S.P® spectrophotometer equipped with SiC Globar source and a DTGS detector, and a Bruker Vertex70® spectrometer coupled to a Hyperion® microscope equipped with a cryogenic mercury–cadmium telluride (MCT) detector. With the Nicolet instrument, 64 scans were acquired on the samples mounted in KBr pellets, in the 4,000–400 cm^{-1} spectral range with a 4 cm^{-1} resolution, and the spectra were processed using the software OMNIC 7.3.94. For measurements with the Bruker Vertex70® spectrometer, the samples were placed between the windows of a diamond anvil cell and observed, with a 30× objective, 128 scans, and a spectral resolution of 4 cm^{-1} .

1997. A sample, approximately 1.8 cm in length, that was detached from the bottom edge of the painting and that was analyzed for the present study is also shown

Table 1 Sample description

Sample	Color	Description
1 ^a	Black	Black material (10 mm×15 mm) covered by a thin layer of white paint
2 ^a	Pale pink	Pale pink material (10 mm×13 mm) with little brown spots on the surface
3 ^a	Pale yellow	Pale yellow material (15 mm×20 mm)
4 ^a	Pale yellow	Pale yellow material (18 mm×22 mm) partially covered with black paint
5 ^a	Black	Black material (14 mm×20 mm) covered by granular material of a light color
6 ^b	Black, pink, green/yellow	Black material (19 mm×9 mm) with green and pink spots
7 ^c	Brown	Drop-like shape (3 mm×3 mm)
8 ^c	Brown	Brown earthy material (7 mm×5 mm)
9 ^c	Semitransparent	Tacky material (7 mm×3 mm)
10 ^c	Off-white	Off-white solid material (7 mm×3 mm)

^a Sample from the strip

^b Sample from *Bohemia Lies by the Sea*

^c Sample from *Die Größe Fracht*

Total reflectance (TR) FTIR spectra in the 7,500–375 cm⁻¹ range were acquired with a Bruker Optics ALPHA spectrophotometer, equipped with a SiC Globalbar source and a DTGS detector. Spectra (128 scans with 4 cm⁻¹ resolution) were processed using the software OPUS 7.0.122. The Kramers–Krönig (KK) algorithm was applied in the 4,000–375 cm⁻¹ range to rebuild absorbance spectra.

Raman spectroscopy

Raman microspectroscopy analyses were carried out with a Renishaw System 1000 configured with a Leica DM LM microscope, notch filters, and a thermoelectrically cooled charged-coupled device (CCD) detector. A 785 nm laser line was used for excitation and was focused on the different areas of the samples using the 50× objective lens of the microscope attached to the spectrometer, achieving a lateral resolution of ~2–3 μm. In order to avoid changes of the sample materials due to overheating, neutral density filters were used to set the laser power at the samples to values between 0.2 and 1.0 mW. A 1,200 lines/mm grating was used and integration times were set between 10 and 300 s. The wavenumber stability and the accuracy were checked by recording the Raman spectrum of a silicon wafer (520 cm⁻¹).

X-ray diffraction

Two powder samples were investigated by X-ray diffraction (XRD) using a Philips X-ray diffractometer 1979 (40 kV, 24 mA) with Cu Kα radiation (λ=1.5406 Å).

Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (¹H NMR) spectra were recorded with a Varian VXR 200 spectrometer operating at a frequency of 199.985 MHz. For these experiments, three powder samples from the strip were subjected to a chloroform (10 ml) extraction at room temperature under magnetic stirring for 30 min. After the removal of the insoluble fraction by filtration on paper, the filtrates were dried at 30 °C with reduced pressure in a Büchi rotavapor. The residues were analyzed by ¹H NMR using deuteriochloroform (CDCl₃) as solvent. The spectra were processed using the software iNMR 3.3.7.

Gas chromatography-mass spectrometry

For the GC/MS analysis, a portion of sample (~0.5 mg) was subjected to saponification assisted by microwaves in 300 μl of KOH in EtOH 10 wt.% at 80 °C for 60 min. The solution was acidified with HCl 6 M and then extracted with diethyl ether (200 μl, three times). The extract was evaporated to dryness under a nitrogen stream and subjected to derivatization with 20 μl of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA), 200 μl of isooctane, and 5 μl of tridecanoic acid solution at 60 °C for 30 min; 5 μl of hexadecane solution were added just before injection (Andreotti et al. 2006).

The GC/MS instrumentation used consisted of a Trace GC 2000 chromatographic system equipped with a PTV injection port and coupled to an ITQ 900 ion trap (Thermo Quest, USA).

Samples were injected in splitless mode at 280 °C. GC separation was performed on a fused silica capillary column HP-5MS (J&W Scientific, Agilent Technologies, USA,

stationary phase 5 % diphenyl-95 % dimethyl-polysiloxane, 30 m, 0.25 mm i.d., 0.25 μm film thickness). The conditions for the chromatographic measurements were as follows: 80 °C initial temperature, 2 min isothermal, 10 °C/min up to 200 °C, 4 min isothermal, 6 °C/min up to 280 °C, 40 min isothermal. The helium (purity 99.9995 %) gas flow was set in constant flow mode at 1.2 ml/min. The MS parameters were as follows: electron impact ionization (EI 70 eV) in positive mode; ion source temperature 230 °C; scan range 50–700 m/z ; interface temperature 280 °C. Peak assignments were based on comparisons with library mass spectra (NIST 1.7, WILEY275).

Pyrolysis gas chromatography-mass spectrometry

Analytical pyrolysis was performed directly on portions of the samples (~0.5 mg) without any pretreatment, using 1,1,1,3,3,3-hexamethyldisilazane (HMDS, chemical purity 99.9 %, Sigma–Aldrich Inc., USA) as a silylation agent for the in situ thermally assisted derivatization of pyrolysis products. The instrumentation consisted of a 5150 CDS Pyroprobe 5000 Series pyrolyzer with a platinum filament coil connected to a gas chromatograph 6890 Agilent (USA) equipped with an HP-5MS fused silica capillary column (stationary phase 5 % diphenyl-95 % dimethyl-polysiloxane, 30 m \times 0.25 mm i.d., Hewlett Packard, USA) and with a deactivated silica pre-column (2 m \times 0.32 mm i.d., Agilent J&W, USA). The GC was coupled with an Agilent 5973 Mass Selective Detector operating in electron impact mode (EI) at 70 eV.

The pyrolysis temperature was 550 °C and was carried out for 20 s. Similar amounts (ca. 100 μg) of sample and HMDS

(7 μl) were inserted into the center of the pyrolysis quartz tube with glass wool. Chromatographic conditions were as follows: initial temperature 32 °C, 10 min isothermal, 10 °C/min to 280 °C, 2 min isothermal, 15 °C/min to 300 °C, and 30 min isothermal. Carrier gas: He (purity 99.995 %), constant flow 1.0 ml/min.

Pyrolysis products were identified by comparing their mass spectra with spectra reported in the Wiley and NIST libraries and with spectra acquired on reference materials.

Imaging

UV fluorescence images were recorded using a Nikon D70 camera and two special low-wattage compact fluorescent lamps emitting long wave UV radiation (Philips PL-S 9 W/08 2P). To avoid the visible component of the light, a DUG11 filter was mounted on the lens.

3. Results and discussion

The analytical results obtained in the samples from each of the three paintings are summarized in Table 2 and are discussed in detail below.

The strip

The surface of the strip was photographed under visible and UV (365 nm) illuminations for documentation purposes as well as to better define the sampling areas (Aldrovandi and

Table 2 Summary of the results obtained in each sample analyzed for the present study

Sample	FORS	FT-IR	Raman	XRD	¹ H NMR	GC/MS	Py-GC/MS
1 ^a	TiO ₂ rutile	Magnetite, TiO ₂ rutile, calcite	TiO ₂ rutile, calcite	Magnetite	Aged drying oil	Aged drying oil	Styrene–butylacrylate copolymer, drying oil
2 ^a	TiO ₂ rutile	TiO ₂ rutile, calcite	TiO ₂ rutile, calcite		Aged drying oil	Aged drying oil	Drying oil
3 ^a		TiO ₂ rutile, calcite, BaSO ₄			Aged drying oil	Aged drying oil	Styrene–butylacrylate copolymer, drying oil
4 ^a	TiO ₂ rutile; ZnS	TiO ₂ rutile, calcite, BaSO ₄	TiO ₂ rutile, calcite, BaSO ₄				
5 ^a		Quartz, kaolinite					
6 ^b		Calcite, dolomite, shellac, Prussian blue	Calcite, dolomite, PB15:3, PO 5, carbon-based black			Drying oil	Drying oil
7 ^{bc}		Shellac					Shellac
8 ^{bc}		Muscovite, kaolinite, nitrates		Muscovite, quartz, kaolinite			
9 ^{bc}		Polyvinyl acetate, plasticizers					Styrene–polyvinyl acetate copolymer
10 ^{bc}		Calcite				Drying oil, shellac	

^a Sample from the strip

^b Sample from *Bohemia Lies by the Sea*

^{bc} Sample from *Die GröÙe Fracht*

Piccolo 2007). The visible images permitted to identify four principal paint areas distributed throughout the object. Their colors ranged from black and pale pink to pale yellow. The area located near the edge of the strip was characterized by a granular surface texture. A single sample was collected from each area with the exception of the pale yellow from which two contiguous fragments were removed (Fig. 1 and Table 1). Several metal staples applied by the artist over the paint surface were also observed (Fig. 4).

The UV examination of the strip allowed to visualize and localize florescent spots or ‘stains’ on its surface that looked organic in nature (Fig. 5).

These stains were generally found to be extremely thin; the removal of a sample from an area where this material appeared to be present in a relatively thicker deposit was done using a cotton swab soaked in acetone. The dried residue obtained from the swab was analyzed in a KBr pellet by FTIR in the transmission mode and shellac was identified by its characteristic absorptions (2,927, 2,855, 1,737, 1,716, 1,640, 1,463, 1,377, 1,247, and 720 cm^{-1}) (Derrick et al. 1999) and by comparing it to a reference spectrum (Fig. 6) in the IRUG 2007 database (IRUG reference INR00273, www.irug.org). Py-GC/MS analysis of a small sample collected from the surface of the same area showed the presence of butolic acid, characteristic molecular marker for shellac resin (Bonaduce et al. 2003). TR FTIR spectra were also acquired in situ on the surface of the strip on various dense stains. All the spectra consistently indicated the presence of shellac (Fig. 6). The shellac was most likely applied as a coating, overall or in certain areas, by the artist.

The 350–2,200 nm FORS spectra of the samples 1 (white film on the surface), 2, and 4 showed the typical features of titanium dioxide (TiO_2) in its rutile form, that has an inflection point at 400 nm in its first derivative spectrum (Piccolo et al. 2007). The reflectance spectrum of sample 4 had, in addition, two absorption bands at 728 and 670 nm that are typical of Co^{2+} ion in pseudo-tetrahedral sulfur coordination in zinc



Fig. 4 Detail of the Strip showing two metal staples

sulfide (ZnS ; Weakliem 1962). In fact, these spectral features are characteristic of zinc sulfide-based compounds, such as lithopone, produced after the mid-1920s (van Alphen 1998, 41–43; Fig. 7a). The presence of ZnS in this sample was confirmed by its FORS spectrum in the 270–800 nm range. The typical strong absorption in the UV region below 350 nm with an inflection point at 340 nm ascribable to ZnS was observed in this sample (Piccolo et al. 2007; Fig. 7b).

These results were further confirmed by FTIR and Raman analysis. The vibrational spectra acquired in samples 2, 4, and on the white surface of sample 1 showed bands due to rutile at ca. 600 and 523 cm^{-1} in the IR and at ca. 143, 448, and 609 cm^{-1} in the Raman spectra. Barium sulfate (BaSO_4) was detected in sample 4 through its IR bands at ca. 1,187, 1,124, 1,077, 982, 637, and 611 cm^{-1} and its most intense Raman feature at ca. 989 cm^{-1} . In this sample, the Raman bands expected for BaSO_4 at ca. 454 and 464 cm^{-1} were masked by the more intense feature of rutile at ca. 448 cm^{-1} (Burgio and Clark 2001). In all the samples analyzed, calcite was identified by its IR bands at 2,520, 1,794, 1,429, 876, and 712 cm^{-1} and by its Raman peaks at ca. 155, 281, 713, and 1,087 cm^{-1} .

Furthermore, in all the FTIR spectra recorded, the presence of an organic material with bands at ca. 2,925, 2,850, and 1,742 cm^{-1} was observed; however, this compound could not be unambiguously identified by this technique. The presence of a silicate-based sand, macroscopically visible over the surface of the entire upper end of the strip, was confirmed by FTIR. The IR spectrum acquired on sample 5, containing grains from the surface, showed spectral features characteristic of crystalline quartz (SiO_2) and of an alumino-silicate (kaolinite) (Gadsden 1975; Fig. 8).

To further characterize the organic materials detected in the FTIR spectra, chloroform extracts from samples 1, 2, and 3 were analyzed by ^1H NMR using deuteriochloroform (CDCl_3) as solvent. In all cases, a drying oil was detected. Due to the relatively low intensity of the NMR signals attributed to the protons in the double bonds and in the methylene groups in α -position to the double bonds, it can be stated that the drying oil has aged considerably (Table 3).

^1H NMR results were confirmed by the FTIR analysis of the extracts. In the case of samples 1 and 2, the FTIR spectra showed, besides the bands characteristic of glyceric esters (between 3,000 and 2,700 cm^{-1} , and at ca. 1,734 cm^{-1}), features due to the OH group (in the range between 3,300 and 2,500 cm^{-1}), and due to the C=O group stretching of the free fatty acids that derive from the hydrolysis of triglycerides (ca. 1,717 cm^{-1}).

In sample 3, no IR bands due to free fatty acids were detected but, in addition to the C=O stretching of the ester, the spectrum showed a broad absorption centered at 1,595 cm^{-1} which can be attributed to the CO_2^- asymmetric stretching of carboxylate ions.

Fig. 5 Images acquired with visible (*left*) and UV (*right*) illuminations, respectively, of an area of the strip located near the right edge (Fig. 1)



The black insoluble fraction of sample 1 showed a peculiar behavior: it was attracted by a magnetic stirrer such as a ferromagnetic compound would. This black powder was analyzed by XRD and FTIR and identified as magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$, CI 77499/Pigment Black 11; Hunt et al. 1995; Gadsden 1975).

It was not possible to identify the pigment responsible for the light yellow color in samples 3 and 4. It is assumed that the artist added a yellow colorant to the white pigment in extremely small quantities causing it to be below the detection limits of the techniques used.

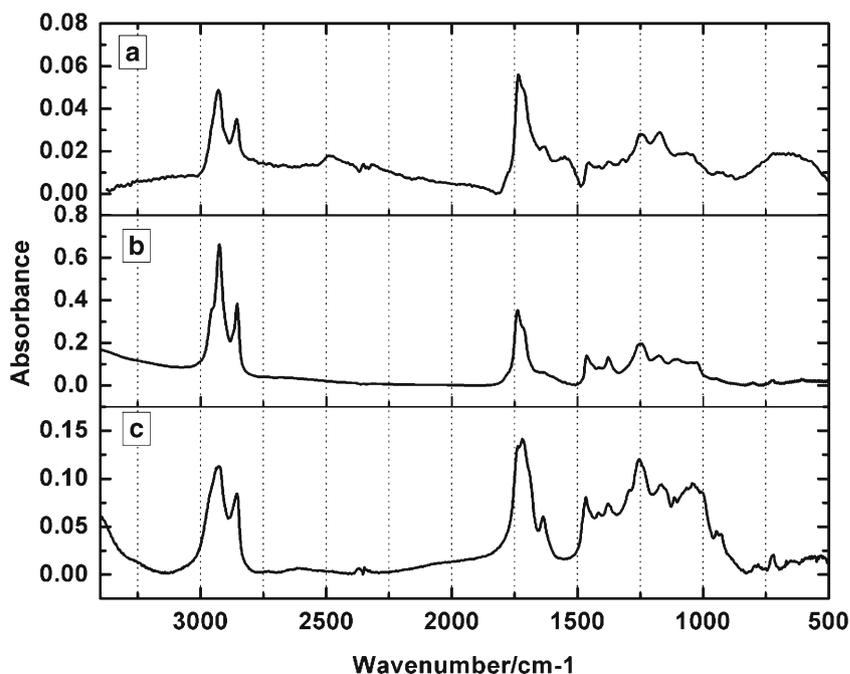
The chemical composition of the organic binders present in the strip paint materials were further investigated by GC/MS and Py-GC/MS analyses performed on portions of samples 1, 2, and 3. GC/MS after saponification and derivatization showed the presence of similar amounts of fatty acids in the three samples. The abundance of azelaic acid and of other dicarboxylic acids was a clear indication that the lipid material was a drying oil, as suggested by the FTIR measurements. Table 4 shows the characteristic chemical parameters used for the interpretation of the fatty acid profile in the samples

analyzed by GC/MS (Andreotti et al. 2006; Colombini et al. 2010).

The value of the palmitic to stearic acid ratio (P/S) has been reported as characteristic of the botanical origin of drying oils. For example, in this case, the observed value of 2.5 suggests the possible presence of walnut oil in the paint, if the oil contained in the paint has a single botanical origin (Colombini et al. 2009). However, P/S is a poor indicator in the case of oil mixtures that can be present in commercial paints (Shilling et al. 2007). Moreover, during his visit to Anselm Kiefer's Studio, Antonio Rava observed large buckets of paint, rather than paint tubes; therefore, it is unlikely that he could have used walnut oil.

The high values of the azelaic acid to palmitic acid ratios (A/P) and of the total percentage of dicarboxylic acids (ΣD) (Table 4) clearly indicate the siccative nature of the lipidic material (Colombini et al. 2010). In particular, A/P is expected to be 1 or higher and ΣD to be above 40 % for a completely cured siccative oil. This is because dicarboxylic acids, such as suberic acid (octandioic), azelaic acid (nonandioic), and sebacic acid (decandioic), are formed as oxidation products of unsaturated fatty acids contained in drying oils during

Fig. 6 FTIR spectra acquired in the 'stains' on the surface of the strip (shown in Fig. 4). Spectrum **a** corresponds to a spectrum acquired in a 'stain' in situ, after the application of the Kramers–Kronig algorithm, spectrum **b** to an acetone extract of a sample removed with a cotton swab, and spectrum **c** to a shellac reference spectrum from the IRUG 2007 database (ref. INR00273)



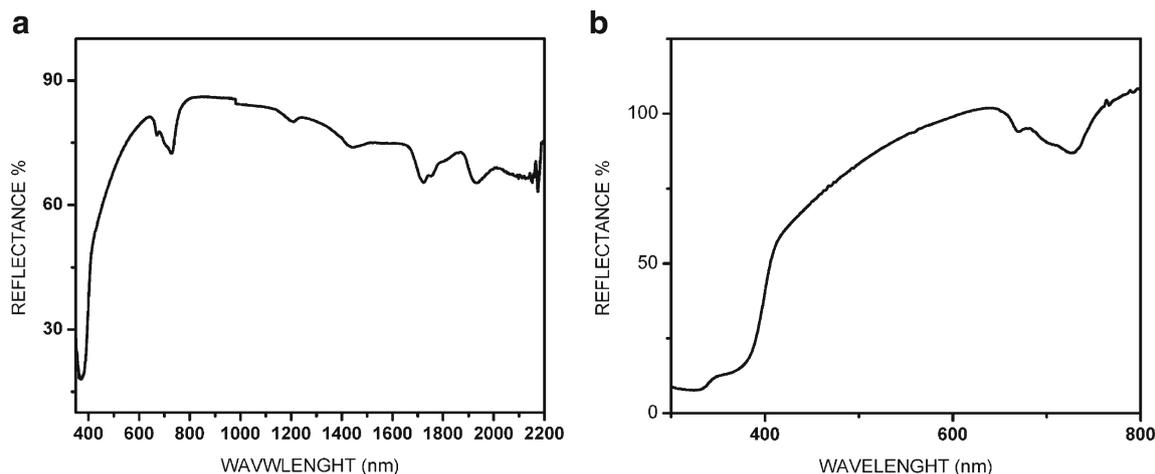


Fig. 7 FORS spectra of sample 4, removed from the strip, confirming the presence of lithopone ($\text{ZnS}+\text{BaSO}_4$). Spectrum a 350–2,200 nm; spectrum b 270–800 nm

curing and ageing. The different samples from the strip showed a different degree of oxidation/curing of the oil: in sample 1, the curing/oxidation processes were less advanced than in samples 2 and 3. The oleic to stearic acid ratio (O/S) is also indicative of the degree of oxidation in terms of the tendency of the double bond of oleic acid to react with oxygen, causing a decrease in the amounts of this acid during oxidation. O/S was indeed higher in sample 1, where oleic acid was found to be present, than in samples 2 and 3, where the content of residual oleic acid was negligible. Since all the samples analyzed represented the full paint layering, from the surface to the canvas support, the lower oxidation degree of sample 1 can be explained by the fact that in the area where the sample was removed from, the paint was thicker and therefore less exposed to oxidation.

Py-GC/MS analyses were also performed in the three samples removed from the strip in order to get information on the presence of synthetic polymers in the paint materials that were not accessible by GC/MS. In samples 1 and 3, acryl–styrene resin peaks were observed as well as those of glycerolipidic materials. These compounds were not detected in sample 2.

This led us to hypothesize that a paint containing a styrene–butylacrylate copolymer was applied only in some areas of the strip (Learner 2004; Scaroni and Chiantore 2009).

Bohemia Lies by the Sea

In the sample from *Bohemia Lies by the Sea*, which consisted of a thick piece of impasto with black, orange, blue, white, pink, and green/yellow paints (sample #6, Table 1). Raman analysis focusing in the white, pink, and yellow paints showed the presence of dolomite, $\text{CaMg}(\text{CO}_3)_2$, with an intense Raman band at $1,098\text{ cm}^{-1}$ (Farmer 1974), indicating that this white compound was mixed with red and yellow colorants. The red and yellow colorants were found to be below the detection limit of the technique under the experimental conditions used.

The synthetic organic pigments Phthalocyanine blue PB 15:3 and Hansa orange PO 5 (Fig. 9) were identified in the blue and orange paints (Fig. 10) (Scherrer et al. 2009), respectively, and a carbon-based black pigment, calcite, and dolomite were found to be present in the black paint.

Fig. 8 On the left, a detail of the Strip showing the location of silica sand; on the right, the FT-IR spectrum of sample 5 showing the absorption bands of quartz and kaolinite

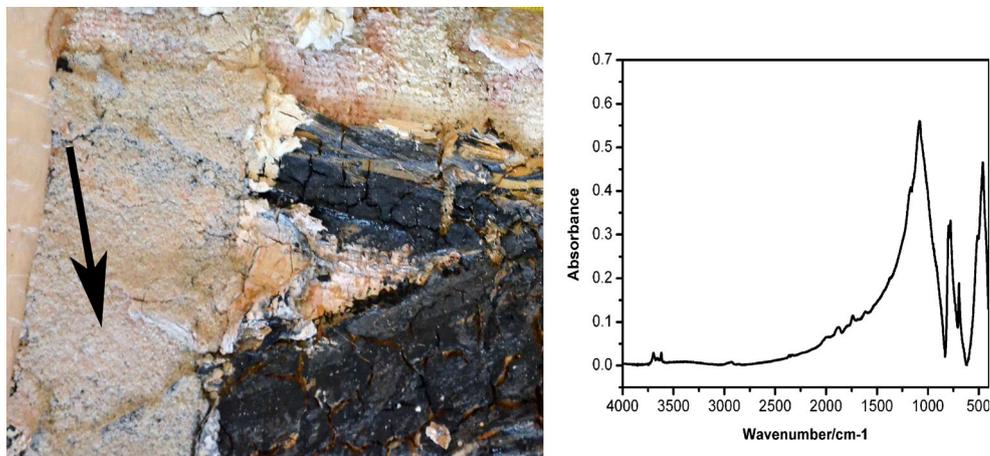


Table 3 ^1H NMR chemical shifts of the chloroform extracts in samples 1, 2, and 3

Frequencies (ppm)	Attribution
5.33	CH of residual double bonds
4.15	CH ₂ glyceric residue
2.34	CH ₂ in α -position to carbonyl
2.02	CH ₂ in α -position to double bonds
1.61	CH ₂ in β -position to carbonyl
1.25	CH ₂ chain
0.87	CH ₃ terminal

FTIR analysis of a small black sample removed from the fragment consistently showed calcite and dolomite (ca. 2,520, 1,800, 1,430, 875, 730, and 712 cm^{-1}), along with shellac (characteristic doublet at ca. 1,715 and 1,735 cm^{-1} and CH stretches at ca. 2,931 and 2,855 cm^{-1} ; Derrick et al. 1999), Prussian blue (2,094 cm^{-1}), and probably a carbon-based black. No bands due to the phosphate group that could indicate whether a bone or an ivory black was used were detected by Raman or FTIR in the black paint.

The GC/MS analysis of this sample showed the presence of a drying oil. The characteristic chemical parameters are reported in Table 4. The P/S value of 1.5 observed in this sample is attributable to linseed oil. The values of A/P and of dicarboxylic acid revealed that the degree of curing was advanced, even if a consistent amount of oleic acid was still present.

Die Größe Fracht

Sample 7 had a brown color, a glassy consistency, and a drop-like shape. A material with a similar appearance is observed over the surface of the artwork, particularly in the paint cracks. FTIR spectra acquired in this sample had all the characteristic absorption bands of shellac (Derrick et al. 1999). Py-GC/MS analysis showed the presence of butolic acid, a marker for shellac resin (Bonaduce et al. 2003), confirming the presence of the compound.

Sample 8 was removed from the thick paint layer with large cracks intended by the artist (Fig. 3) from a spot at the lower

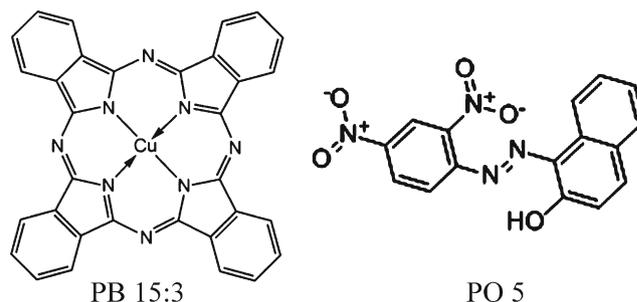
Table 4 Ratios between the contents of palmitic acid and stearic acid (P/S), azelaic acid and palmitic acid (A/P), oleic acid and stearic acid (O/S), and percentage abundance of dicarboxylic acids (ΣD), as determined by GC/MS in the samples analyzed

Sample	P/S	A/P	O/S	ΣD
1 ^a	2.5	0.6	1.0	26
2 ^a	2.4	1.0	0.2	41
3 ^a	2.9	1.1	0.5	43
6 ^b	1.5	1.4	2.3	39
10 ^c	1.5	1.4	0.2	48

^a Sample from the strip

^b Sample from *Bohemia Lies by the Sea*

^c Sample from *Die Größe Fracht*

**Fig. 9** Chemical structures of Phtalocyanine bleu (PB 15:3) and Hansa Orange (PO 5)

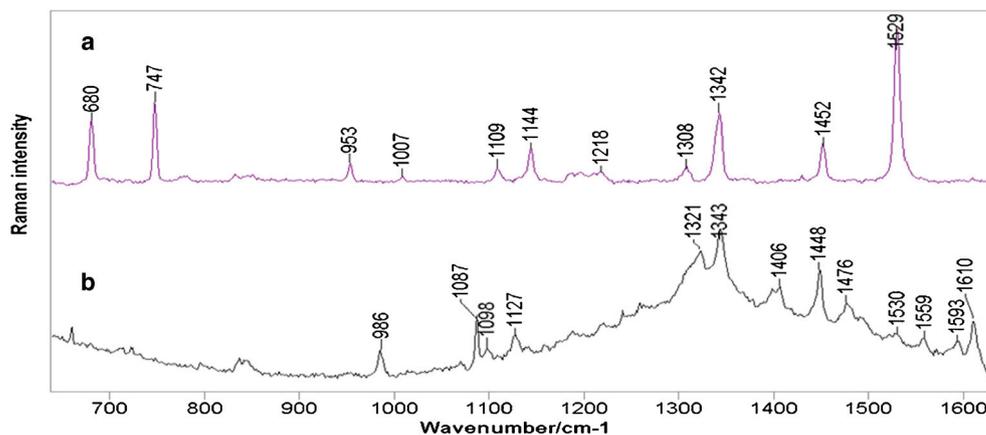
edge of the work. This layer is quite fragile, so the paint detached easily. The analysis of this sample revealed the presence of the inorganic compounds muscovite, quartz, nitrates, and a small amount of kaolinite, a composition that corresponds to a typical clay, but no organic materials were detected. In this sample, all muscovite characteristic bands were observed in the FTIR spectrum recorded (ca. 3,625, 1,076, 1,025, 926, and 748 cm^{-1}), which also matched reference spectra in the IRUG 2007 database (IMP00112 muscovite mica, KMG Minerals Inc., U-125, PMA, tran). Kaolinite was easily identified in the sample by its IR bands at ca. 3,695, 3,620, 1,100–900, 796, 748, 695, 468, and 432 cm^{-1} . These bands were found to be consistent with those observed in the spectrum recorded in a kaolinite reference sample provided by the Department of Mineralogy of the University of Pisa. In the FTIR spectrum recorded in sample 8, a peak at 1,384 cm^{-1} that can be assigned to a nitrate was also observed. Even though bands expected for quartz were not visible in the FTIR spectrum acquired, this compound was observed by XRD analysis, along with muscovite, and minor amounts of other minerals (most probably kaolinite) that are typical of clays.

The material in sample 9 was tacky and it was observed over all the surface of the artwork but mainly in the paint cracks. The FTIR analysis of this sample suggested the presence of a synthetic resin composed of polyvinyl acetate (PVAc) with characteristic absorption bands at ca. 2,969, 2,875, 1,738, 1,434, 1,372, 1,245, 1,020, 947, 794, and 605 cm^{-1} (Fig. 11; IRUG 2007 database; ISR00130 poly(vinyl acetate), PVAc, Vinac, WM). Other bands at ca. 1,600 and 1,580 cm^{-1} in the IR spectrum recorded are probably due to additives and plasticizers (such as diethylphthalate) in the glue formulation.

Py-GC/MS analysis was performed to further characterize the components in sample 9. The pyrolysis profile of the sample and the relative peak assignments are shown in Fig. 12.

We observed the presence of acetic acid, marker of polyvinyl acetate resin (PVAc), and styrene. The relatively high amount of styrene suggests that this product derives not only from the pyrolysis of the PVAc. The presence of these markers and of styrene oligomers permitted to identify the material as

Fig. 10 *Bohemia Lies by the Sea*. Raman spectra of the *blue* (spectrum **a**) and *orange* (spectrum **b**) paints in the impasto, showing the presence of the synthetic organic pigment PB 15:3 and of PO5 mixed with calcite, respectively. $\lambda_0=785$ nm



copolymer styrene/polyvinyl acetate used as a hot melt adhesive. The intense diethylphthalate peak observed was derived from a plasticizer used in the adhesive formulation to decrease its softening point (Learner 2004; Scalarone and Chiantore 2009).

Fragment 10 was collected from the frame on the left edge of the artwork. FTIR analysis revealed that its principal component is calcite. Bands due to an organic binder were also visible at ca. 2,980, 2,830, and 1,740 cm^{-1} . The composition of the organic binder in this sample was further investigated by GC/MS. The chromatogram of the lipid and resinous fraction of the sample, obtained after saponification and derivatization, showed the presence of linear monocarboxylic acids with an even number of carbons, being palmitic and stearic acids the most abundant. Dicarboxylic acids were also detected, with nonandioic acid (azelaic acid) being the most abundant. The P/S, A/P and O/S ratios obtained (Table 4) were compared with the average values calculated for reference paints in the literature (Colombini et al. 2010). The high value of the A/P ratio, together with the amount of dicarboxylic

acids detected, clearly demonstrates the siccative nature of the lipidic material (probably linseed oil). Finally, the identification of shelloic acid, butolic acid, and aleuritic acid confirmed the presence of shellac in the sample (Bonaduce et al. 2003).

Conclusions

Using microsampling and noninvasive techniques, we characterized and identified some of the materials used by the contemporary artist Anselm Kiefer in three works: a large strip cut by the artist in the 1990s from a polymateric painting on canvas, the painting *Bohemia Lies by the Sea*, in the collection of The Metropolitan Museum of Art (New York, USA), and the work *Die GröÙe Fracht*, in the collection of the San Giorgio Library (Pistoia, Italy). The data presented highlights the originality and diversity of the materials used by the artist.

In addition to pigments in common use in the twentieth century, such as carbon-based black, titanium white (TiO_2 , rutile), lithopone ($\text{ZnS}+\text{BaSO}_4$), and the synthetic organic pigments PB 15:3 and PO 5, and other less frequently reported components such as magnetite (Fe_3O_4), silica sand, and metal staples, were observed. Molecular analysis of the organic components revealed the use of drying oils as binders in the three works. The glycerolipid materials had similar compositions in the paintings *Bohemia Lies by the Sea* and *Die GröÙe Fracht* and appeared to match the pattern of linseed oil. The polymateric fragments in the strip also contained drying oil paints but with a different fatty acid profile, suggesting a different oil mixture in the paints. The high P/S ratio observed in the paint in this work could be associated with the presence of walnut oil, however, as stated above, these ratios are poor indicators of the botanical origin of oils in mixtures that can be present in commercial paints. A synthetic paint based on a styrene copolymer was also detected in selected areas of the strip.

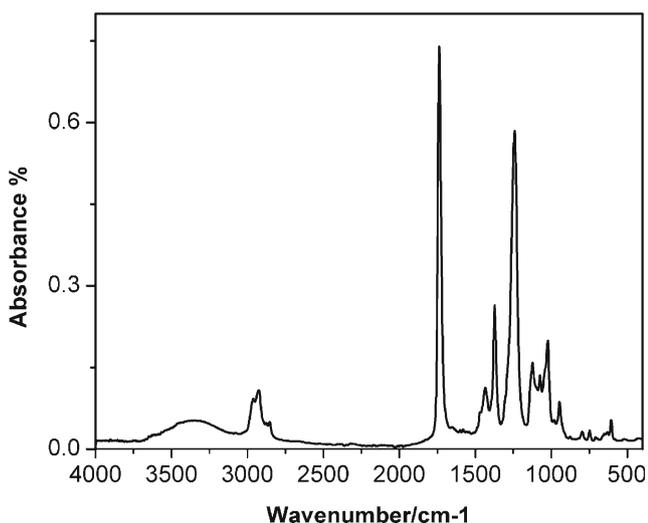
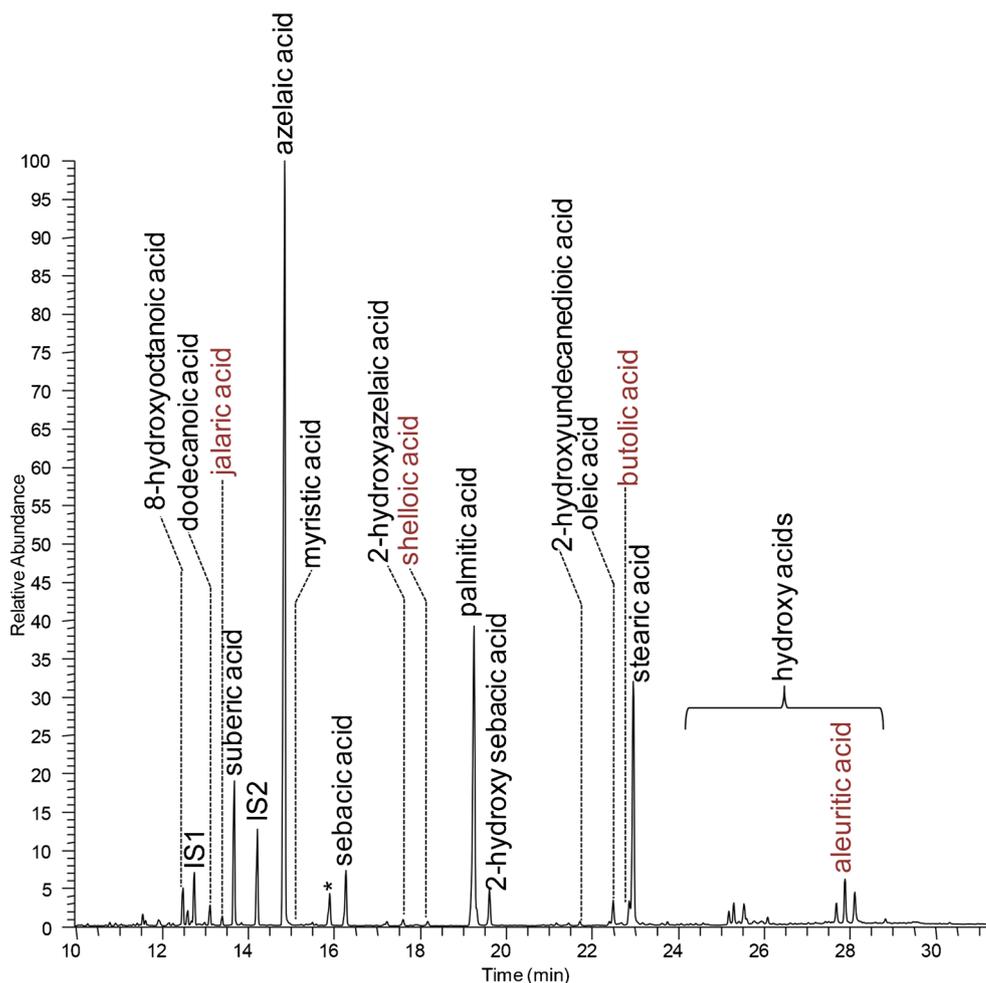


Fig. 11 Ft-IR spectrum of sample 9 showing the spectral features of polyvinyl acetate (PVAc)

Fig. 12 GC/MS chromatogram of sample 10, taken from *Die Größe Fracht*. IS1 internal standard hexadecane, IS2 internal standard tridecanoic acid, * phthalate contaminant. The compounds bringing hydroxyl and carboxylic groups are separated as TMS ethers and esters



Shellac was detected in surface areas on the strip, on the surface of *Die Größe Fracht*, in the form of brown drops, and in the sample from *Bohemia Lies by the Sea*. The role of shellac in Kiefer's work is emblematic because it is one of the materials that he praises the most for the glossy appearance and amber color that it confers, and for its good adhesion to other materials. Kiefer used to pour it as a liquid on the surface of the works, from which it infiltrated the lower paint layers, like he later did by pouring liquid metal onto the surface of the paint and letting it permeate the stratigraphy of the paintings. Shellac is known to become brittle with aging, and its presence in generous layers not only on top but also between and within the paint layers will sometimes result in a failing bond between them. Spontaneous losses that occurred on *Bohemia Lies by the Sea*, for instance, appear to be symptomatic of that deterioration process. Additionally shellac also tends to darken much over time, which will then affect the original color relationships of a work of art. But as we know, this particular change is welcomed by Kiefer. In all the works examined for the present study, shellac was used by the artist rather than being the result of a restoration intervention.

Anselm Kiefer chooses his materials moved by his inspiration and special needs. This is why it is not possible to predict what the composition of his works are, nor to establish a priori, without in-depth examination and analysis how certain materials were applied. Nevertheless, we can assert that the use of siccative oils, such as linseed and other drying oils, and their mixture with synthetic polymers, such as acrylic enamels, due to a need for quick drying, are common in his works. Kiefer, like many other twentieth century artists, discovered that pictorial layers can set rapidly by adding compatible synthetic resins instead of waiting for the oils to set. In the works that we examined for the present study, some areas appear dry and others glossy depending on the binder mixtures present, and oil dripping may have occurred in the years after the works were finished due to the nonperfect mix of the oil and the synthetic polymers. These can be considered normal consequences of the technique used by the artist, even if not intended by him. Kiefer has expressly stated that he accepts changes to the pictorial layers which could occur over time.

In the interview that Anselm Kiefer had with Antonio Rava (published with the permission of the artist in the book "Conserving Contemporary Art: Issues, Methods, Materials,

and Research”, now translated into English; Chiantore and Rava 2013), he explained that he accepts that some parts of his works may crack and fall over time, and he states he exposes his paintings to the outdoor environment, also in Winter, with the express purposes to accelerate the process of seasoning and decay of the surfaces and to give a more used and historicized aspect to the paint. It can be said that, in general, these paints are firmly bound, except in the outer surfaces.

Since the interview with Antonio Rava took place in 2000, a number of studies on paintings by Kiefer were undertaken (Hale and Witkin 2012; Lauterwein 2008; Rampley 2000; West and Dougherty 2011), and there is now a deeper knowledge of his intentions, materials, and techniques, as often researchers involve the artist to explain his ideas and clarify issues. We hope that the present work contributes to an increased understanding of why Kiefer’s work looks the way they do today and what can be done to best conserve and preserve them, especially in view of assessing, as part of COPAC project, future interventions.

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References

- Albano AP (1998) Reflections on painting, alchemy, nazism: visiting with Anselm Kiefer. *JAIC* 37(3):348–361
- Aldrovandi A, Picollo M (2007). *Metodi di documentazione e indagini non invasive sui dipinti*. Collana I Talenti, Il Prato eds., Padova, pp 67–83
- Andreotti A, Bonaduce I, Colombini MP, Gautier G, Modugno F, Ribechini E (2006) A combined GC-MS analytical procedure for the characterisation of glycerolipid, waxy, resinous and proteinaceous materials in a unique paint micro-sample. *Anal Chem* 78: 4490–4500
- Bacci M, Boselli L, Picollo M, Radicati B (2009) UV, VIS, NIR fibre optic reflectance spectroscopy (FORS). In: Pinna D, Galeotti M, Mazzeo R (eds) *Practical handbook on diagnosis of paintings on movable support*. European Project ARTECH, Centro Di, Firenze, pp 197–200
- Bonaduce I, Colombini MP, Gautier G (2003) Molecular pattern recognition of fresh and aged shellac. *Chromatographia* 58:357–364
- Burgio L, Clark RJH (2001) Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation. *Spectrochim Acta Part A Mol Biomol Spectrosc* 57(7):1491–1521
- Cacciari M, Celant G (1997) *Anselm Kiefer*. Catalogo della mostra (Venezia, Museo Correr 1997), Charta, Milano
- Calabrese O, Corà B (2007) *Anselm Kiefer*. Die Grosse Fracht, Gli Ori, Pistoia
- Celant G (2008) *Kiefer e Mao: che mille fiori fioriscano*. Skira, Milano
- Chiantore O, Rava A (2005) *Conservare l’arte contemporanea*. Problemi, metodi, materiali, ricerche. Electa, Milano
- Chiantore O, Rava A (2013) *Conserving contemporary art: issues, methods, materials, and research*. The Getty Conservation Institute, Los Angeles
- Colombini MP, Modugno F, Ribechini E (2009) Gas chromatography/mass spectrometry in the characterization of lipids. In: Colombini MP, Modugno F (eds) *Organic mass spectrometry in art and archaeology*. John Wiley & Sons Ltd, pp 191–231
- Colombini MP, Andreotti A, Bonaduce I, Modugno F, Ribechini E (2010) Analytical strategies for characterising organic paint media using GC-MS. *Acc Chem Res* 39:715–727
- Derrick MR, Stulik D, Laundry JM (1999) *Infrared spectroscopy in conservation science*. The Getty Conservation Institute, Los Angeles
- Eccher D (1999) *Un’anima oscura*, Art e Dossier, Giunti. Firenze 146:40–45
- Farmer VC (1974) *The infrared spectra of minerals*. Mineralogical Society, London
- Gadsden JA (1975) *Infrared spectra of minerals and related inorganic compounds*. Butterworth & Co Ltd, London
- Griffin A, Young C, Hale T (2014) History is my material. In: Bridgland J (ed) *ICOM-CC 17th triennial conference preprints*, Melbourne, 15–19 September 2014, International Council of Museums, Paris, art. 1305, 11 pp. ISBN 978-92-9012-410-8
- Hale T, Witkin RD (2012) *Sow’s ears and silk purses: maintaining the art works of Anselm Kiefer*. Courtauld Institute of Art White Cube, London
- Hunt CP, Moskovitz BM, Banerjee SK (1995) Magnetic properties of rocks and minerals. In: Ahrens TJ (ed) *Rock physics and phase relations, a handbook of physical constants*. Washington, USA, pp 189–205
- Lauterwein A (2008) Anselm Kiefer/Paul Celan: myth, mourning and memory. *Hyperion* III(3):45–51
- Learner TJS (2004) *Analysis of modern paints*. The Getty Conservation Institute, Los Angeles
- Lindner S, Vitoria A, Alba L (2004) Anselm Kiefer at the Guggenheim Museum Bilbao: towards a new methodology for the preventive conservation of contemporary artworks. In: *Modern Art, New Museums, Contributions To the XX IIC congress*, Bilbao, 13–17 September 2004, pp 21–24
- Piccolo M, Bacci M, Magrini D, Radicati B, Trumpy G, Tsukada M, Kunzelman D (2007) Modern white pigments: their identification by means of non-invasive ultraviolet, visible and infrared fiber optic reflectance spectroscopy. In: Learner TJS, Smithen P, Krueger JW, Schilling M (eds) *The modern paints uncovered symposium*, Tate Modern, London, May 16–19, 2006. The Getty Conservation Institute, Los Angeles, pp 118–128
- Rampley M (2000) In search of cultural history: Anselm Kiefer and the ambivalence of modernism. *Oxf Art J* 23(1):73–96
- Rumma L, Belpoliti M, Andreotti R, De Melis F (2006) *Anselm Kiefer. Merkaba*. I Sette Palazzi Celesti, Di Stefano, Gute Ed., Charter/GVA Milano
- Scalarone D, Chiantore O (2009) Py-GC/MS of natural and synthetic resins, in organic mass spectrometry. In: Colombini MP, Modugno F (eds) *Art and archaeology*. John Wiley & Sons Ltd, pp 327–361
- Scherrer NC, Zumbuehl S, Delavy F, Fritsch A, Kuehnen R (2009) Synthetic organic pigments of the 20th and 21st century relevant to artist’s paints: Raman spectra reference collection. *Spectrochim Acta A* 73(3):505–524
- Schilling MR, Mazurek J, Learner TJS (2007) Studies of modern oil-based artists’ paint media by gas chromatography/mass spectrometry. In: *Modern paints uncovered: proceedings from the modern paints uncovered symposium*. Getty Conservation Institute, Los Angeles, p 129–39
- Van Alphen M. (1998) *Paint film components*. Monograph, general series 2. National Environmental Health Forum, Australia
- Weakleim H (1962) Optical spectra of Ni²⁺, Co²⁺, and Cu²⁺ in tetrahedral sites in crystals. *J Chem Phys* 36:2117–2140
- West JJ, Dougherty N (2011) The palette of Anselm Kiefer: witnessing our imperiled world. *ARAS Journal*. <https://aras.org/sites/default/files/docs/00039WestDougherty.pdf>