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ABSTRACT: The painter, Vincent van Gogh, and some of his contemporaries frequently made use of the pigment chrome yellow that is known to show a tendency toward darkening. This pigment may correspond to various chemical compounds such as PbCrO4 and PbCr1−xSxO4, that may each be present in various crystallographic forms with different tendencies toward degradation. Investigations by X-ray diffraction (XRD), mid-Fourier Transform infrared (FTIR), and Raman instruments (benchtop and portable) and synchrotron radiation-based micro-XRD and X-ray absorption near edge structure spectroscopy performed on oil-paint models, prepared with in-house synthesized PbCrO4 and PbCr1−xSxO4, permitted us to characterize the spectroscopic features of the various forms. On the basis of these results, an extended study has been carried out on historic paint tubes and on embedded paint microsamples taken from yellow-orange/pale yellow areas of 12 Van Gogh paintings, demonstrating that Van Gogh effectively made use of different chrome yellow types. This conclusion was also confirmed by in situ mid-FTIR investigations on Van Gogh’s Portrait of Gauguin (Van Gogh Museum, Amsterdam).

Historical and more recent documentations report that chrome yellow pigments were widely used by Van Gogh1 and his contemporaries.2−4 They are characterized by different
For this purpose, we have synthesized and characterized different crystal forms of PbCrO₄ and PbCr₁₋ₓSₓO₄ (0.1 ≤ x ≤ 0.75) by employing X-ray diffraction (XRD), mid-Fourier Transform infrared (mid-FTIR), Raman, synchrotron radiation-based micro XRD (SR μ-XRD), and S K-edge micro-X-ray absorption near edge structure spectroscopy (μ-XANES). Complementary information was collected by scanning transmission electron microscopy (STEM) equipped with energy dispersive X-ray (EDX) spectrometry. An extended study was carried out on pigments from historic paint tubes and on microsamples from paintings by Van Gogh and his contemporaries. The results demonstrate that it is possible to distinguish among the various orthorhombic and monoclinic forms of PbCrO₄ or PbCr₁₋ₓSₓO₄ and that Van Gogh and his contemporaries effectively made use of these different chrome yellow pigments.

In the companion paper (part 4 of the series), the artificially aged of the aforementioned chrome yellow-based model paints, we demonstrate that different forms of chrome yellows show a strong different tendency toward darkening. To be able to distinguish among these different varieties is therefore very relevant, since it may open up the possibility to investigate whether there is an effective correlation between the chrome yellow composition/crystalline structure and its preservation state in original paintings.

### EXPERIMENTAL SECTION

#### Synthesis of PbCrO₄ and PbCr₁₋ₓSₓO₄ and Preparation of Paint Models

The synthesis of monoclinic PbCrO₄ powder (S₁mono₄ where * denotes pure inorganic powder without an organic binder added) and several PbCr₁₋ₓSₓO₄ solid solutions with increasing x values, (S₁ortho, S₁mon, S₁trans, S₁B, S₁D) was performed following Crane et al.15 while the preparation of orthorhombic PbCrO₄ (S₁ortho) was accomplished according to Xiang et al.15 (see the Supporting Information for further details about the synthesis). Table 1 shows the properties of the synthesized lead chromate-based compounds.

Paint models (S₁−S₃D) were prepared by mixing the powders with linseed oil in a 4:1 weight ratio and applying the mixture on polycarbonate microscopy slides. Employing the same procedure, two further paints were prepared: the first, hereby indicated as D₁, by mixing oil and a commercial pigment (CIBA and BASF), while the other, D₂, was made of oil, PbCrO₄, and PbSO₄.
Table 2. List of the Original Embedded Paint Microsamples and Historic Chrome Yellow Pigments Investigated

<table>
<thead>
<tr>
<th>Origin of paint sample</th>
<th>Sample number/name</th>
<th>Chrome yellow composition</th>
<th>Techniques for detecting the chrome yellow type</th>
<th>PANTONE Hue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Historic oil paint tube belonging to the Dr. Gachet collection (ca. 1890) (Berthault, Paris) (M’O)</td>
<td>DG₁</td>
<td>monoclinic</td>
<td>XRD, Raman, FTIR</td>
<td>(109C)</td>
</tr>
<tr>
<td>Historic oil paint tube (1902-1913) (Mommen &amp; Cie, Brussels) (Royal Museum of Fine Arts, Antwerp)</td>
<td>DG₂</td>
<td>monoclinic</td>
<td>XRD, Raman, FTIR</td>
<td>(130C)</td>
</tr>
<tr>
<td>Historic oil paint tube (end 19th century) (Elsene, Brussels) (Royal Academy of Fine Arts, Antwerp)</td>
<td>A</td>
<td>orthorhombic</td>
<td>XRD, Raman, FTIR</td>
<td>(3945C)</td>
</tr>
<tr>
<td>Bank of the Seine, 1887 (VGM)</td>
<td>B₁</td>
<td>monoclinic</td>
<td>XRD, Raman, FTIR</td>
<td>(108C)</td>
</tr>
<tr>
<td>Grapes, 1887 (VGM)</td>
<td>B₂</td>
<td>monoclinic</td>
<td>XRD, Raman, FTIR</td>
<td>(130C)</td>
</tr>
<tr>
<td>Sunflowers gone to seed, 1887 (VGM)</td>
<td>F293/3</td>
<td>monoclinic</td>
<td>XRD, Raman, FTIR</td>
<td>(109C)</td>
</tr>
<tr>
<td>Self-portrait with straw hat, 1887 (VGM)</td>
<td>F377/2</td>
<td>monoclinic</td>
<td>XRD, Raman, FTIR</td>
<td>(109C)</td>
</tr>
<tr>
<td>Quinces, lemons, pears and grapes, 1887 (VGM)</td>
<td>F469/2</td>
<td>orthorhombic</td>
<td>XRD, Raman</td>
<td>(387C)</td>
</tr>
<tr>
<td>Field with flowers near Arles, 1888 (VGM)</td>
<td>F489/1</td>
<td>monoclinic</td>
<td>XRD, Raman, FTIR</td>
<td>(109C)</td>
</tr>
<tr>
<td>The bedroom, 1888 (VGM)</td>
<td>F482/7</td>
<td>monoclinic</td>
<td>XRD, Raman, FTIR</td>
<td>(1375C)</td>
</tr>
<tr>
<td>The Dance Hall in Arles (&quot;Bell in Arles&quot;), 1888 (M’O)</td>
<td>10872</td>
<td>monoclinic</td>
<td>XRD, Raman, FTIR</td>
<td>(109C)</td>
</tr>
<tr>
<td>Falling leaves (Les Alyscamps), 1888 (KMM)</td>
<td>224/1</td>
<td>monoclinic and possibly orthorhombic</td>
<td>XRD, Raman, FTIR</td>
<td>(945C)</td>
</tr>
<tr>
<td>Portrait of Gauguin, 1888 (VGM)</td>
<td>X448_2</td>
<td>monoclinic and possibly orthorhombic</td>
<td>XRD, Raman</td>
<td>(3645C)</td>
</tr>
<tr>
<td>Sunflowers, 1889 (VGM)</td>
<td>F458/3</td>
<td>monoclinic and possibly orthorhombic</td>
<td>XRD, Raman, FTIR</td>
<td>(395C)</td>
</tr>
<tr>
<td>Tree roots, 1890 (VGM)</td>
<td>F816/3</td>
<td>monoclinic and possibly orthorhombic</td>
<td>XRD, Raman, FTIR</td>
<td>(108C)</td>
</tr>
<tr>
<td>Be mysterious, P. Gauguin, 1890 (M’O)</td>
<td>2751</td>
<td>monoclinic and possibly orthorhombic</td>
<td>XRD, Raman, FTIR</td>
<td>(3945C)</td>
</tr>
<tr>
<td>Van Gogh palette, 1890 (M’O)</td>
<td>10455</td>
<td>monoclinic</td>
<td>XRD, Raman, FTIR</td>
<td>(116C)</td>
</tr>
<tr>
<td>Cézanne palette (M’O)</td>
<td>10426</td>
<td>monoclinic</td>
<td>XRD, Raman, FTIR</td>
<td>(93C)</td>
</tr>
</tbody>
</table>

Note: Monoclinic: PbCr₁₋ₓSₓO₄ is more similar to the reference S₃C. Monoclinic and possible orthorhombic: PbCr₁₋ₓSₓO₄ is more similar to the reference S₃B (see text for details). XRD performed by employing only the portable instrumentation. An indirect semiquantitative estimation of the S amount was also performed by SEM-EDX (Figure S-4 of the Supporting Information). *Mixture of chrome yellow and orange (phoenicochroite (1-x)-PbCrO₄·xPbO). **SR μ-XRD performed at DESY/PETRA III facility (beamline P06) (Hamburg, Germany). ***SR μ-XRD performed at DESY/DORIS III facility (beamline L) (Hamburg, Germany). ****SR μ-XRD and a DESY/DORIS III-beamline L instrument (Hamburg, Germany).

Original Samples. Historic Oil Paint Tubes. In addition to the already investigated historic chrome yellow paints A, B₁, and B₂ belonging to late 19th century artists, two other paint samples (denoted below as DG₁ and DG₂), supplied by the Musée d’Orsay (M’O, Paris, France), were taken from two oil-paint tubes originally belonging to the Dr. Paul Gachet collection, assumed to have been used by Van Gogh. Some of their properties are reported in Table 2 and in the Supporting Information.

Embedded Micropaint Samples. Table 2 also shows some properties and results obtained from the investigation of fifteen micropaint samples from chromium-based yellow areas of twelve paintings by Van Gogh, one by Gauguin, and two other samples from the palettes of Cézanne and Van Gogh; these materials were
Characterization of Paint Models. XRD and HAADF/STEM-EDX. A combination of XRD and HAADF/STEM-EDX mapping were used to determine the morphology, the S and Cr local distributions, and the phase composition of in-house synthesized and commercial PbCr$_x$S$_{3-x}$O$_4$.

Diffraction patterns [Figure 1A (top panel) and Figure S-1 of the Supporting Information] of powders recorded by the benchtop equipment (black) are similar to those collected from the corresponding paint models at the PETRA-III SR-facility (blue). Rietveld refinement (Table 1) indicates that powders S$_{3A}$ and S$_{3D}$ are composed of a single monoclinic phase (a minor amount of orthorhombic PbCrO$_4$ is present in S$_{3B}$). As in the work by Crane et al., the lattice parameters (Table S-1 of the Supporting Information) of each PbCr$_x$S$_{3-x}$O$_4$ phase decrease with increasing S content. This is observable on the recorded patterns (Figure 1A, bottom panel) by a progressive shift of the diffraction peaks toward higher Q values [see e.g., (111) and (020) peaks of the S$_{3A}$ (monoclinic phase)]

While the fraction of monoclinic PbCr$_x$S$_{3-x}$O$_4$ decreases to ca. 60 wt % in S$_{3C}$ and 11.5 wt % in S$_{3D}$, the orthorhombic equivalents (such as PbCr$_{0.1}$S$_{2.9}$O$_4$) become more prevalent (ca. 30 wt % in S$_{3C}$ and ca. 75 wt % in S$_{3D}$). A contribution of 9–14 wt % of orthorhombic PbCrO$_4$ is also present in these samples. In powder D$_{3B}$, although revealing an elemental composition similar to that of S$_{3B}$, monoclinic PbCr$_{1.9}$S$_{1.1}$O$_4$ is the main constituent; the presence of some orthorhombic PbSO$_4$ was also observed.

The combined use of HAADF-STEM (Figure S-2 of the Supporting Information) and STEM-EDX in the investigation of S$_{3B}$ and S$_{3D}$ (Figure 1B and Figure S-2C of the Supporting Information for S$_{3C}$ results) revealed the presence of nanocrystals of two different shapes and elemental composition: Cr-rich elongated rods of variable size (ca. 200–500 nm) and S-rich globular particles (ca. 50 nm diameter). Consistent with the average XRD results (Table 1), literature data, the STEM-EDX quantitative analysis (Figure 1B), the rods correspond to monoclinic phases and the globular particles to orthorhombic ones.

pH measurements of 10 mL of water equilibrated with 1–2 mg of the in-house synthesized powders showed that the orthorhombic PbCrO$_4$ (S$_{3ortho}$) and the monoclinic co-precipitates (S$_{3A}$, S$_{3B}$) yielded a slightly acidic pH value (5.7 ± 0.1), while the PbCr$_{0.2}$S$_{2.8}$O$_4$ materials composed of monoclinic and orthorhombic forms (S$_{3C}$, S$_{3D}$) and PbSO$_4$ yielded a significantly lower pH (4.5 ± 0.1). The monoclinic PbCr$_{0.2}$S$_{2.8}$O$_4$ (S$_{3A}$) featured a slightly higher pH value (6.1 ± 0.1). The pH value obtained for S$_{3ortho}$ is consistent with that of Crane et al. and can be indirectly related to the higher solubility of the orthorhombic PbCr$_{0.2}$S$_{2.8}$O$_4$ (K$_{sp}$ = 10$^{-10.71}$, $\Delta G^0_{\text{orthorhombic}}$ = ~813.2 kJ/mol) compared to that of the thermodynamically more stable monoclinic form (K$_{sp}$ = 10$^{-12.60}$, $\Delta G^0_{\text{monoclinic}}$ = ~824 kJ/mol). Similar conclusions can be drawn for the solubility of orthorhombic PbCr$_{0.2}$S$_{2.8}$O$_4$ relative to their monoclinic equivalents.

S$K$-edge $\mu$-XANES. S$K$-edge $\mu$-XANES spectra of PbCr$_{0.2}$S$_{2.8}$O$_4$ paint models (Figure 1C) are generally similar to that of PbSO$_4$ reference compound, featuring a prominent peak at around 2.482 keV, specific for the sulfate species. However, there are subtle differences when the Cr content decreases in PbCr$_{0.2}$S$_{2.8}$O$_4$: an additional pre-edge feature gradually appears on the left side of the S(VI) peak around 2.481 keV, while several $\Delta G_{\text{orthorhombic}}^0$.
220 postedge features become more clearly defined. Figueiredo et al. observed analogous features in various Fe(II) and Fe(III) sulfate minerals that were related to differences in the symmetry and nature of the S-binding site. The Figure 1C spectra are consistent with the view that in PbSO₄, all sulfate oxygen atoms are directly bound to Pb atoms, giving rise to a simple S(VI) XANES pattern. In the more Cr-rich co-precipitate materials the sulfate groups are more isolated, implying the disappearance of some pre- and postedge features.

Infrared Spectroscopy. Transmission Mid-FTIR. Spectra collected from paint models (Figure 2A) feature some changes when the SO₄²⁻ content increases going from S3A to S3D; additional differences are visible in the spectra of the two polymorph forms of PbCrO₄ (S1mono, S1ortho).

In the ν₃ sulfate asymmetric stretching region, the monoclinic S3A and S3B show a weak signal around 1102 cm⁻¹; this band becomes stronger and moves toward higher wavenumbers (1115 cm⁻¹) in S3C and S3D where orthorhombic phases are present. When going from S3A to S3D, two additional signals around 1165 and 1047 cm⁻¹ [ν₄(SO₄²⁻)] become progressively visible, as well as the IR-forbidden sulfate symmetric stretching mode (ν₁ at 966 cm⁻¹).

The ν₄ sulfate asymmetric bending region is characterized by the presence of two signals at ca. 626–627 and 597 cm⁻¹. With increasing sulfate amount, a shift of the former band to 620–618 cm⁻¹ is observed, while an increase of the relative intensity of the band at 597 cm⁻¹ also takes place.

In the ν₃ chromate asymmetric stretching region (930–800 cm⁻¹), both a band broadening and a shift toward higher wavenumbers is detected when the amount of chromate decreases.

Consistent with the XRD data (Table 1) and studies on other MCr₁₋ₓSₓO₄ (M = Ba, Ca, Sr, Pb, and Na), this is justified by changes in the crystalline structure.

Two bands at 852 and 832 cm⁻¹ are present in the spectra of S1mono and S3A; their position shifts toward highest energies for S3B (855 and 832 cm⁻¹) and S3C (859 and 837 cm⁻¹). For these two latter samples, an additional signal around 885 cm⁻¹ is visible. The spectrum of S3D features a broad band around 865 cm⁻¹ that shifts up to 905 cm⁻¹ for S1ortho. Consistent with the XRD results (Table 1), the spectral features of D1 resemble those of S3C and D2 (the latter showing band features of both monoclinic PbCrO₄ and of orthorhombic PbSO₄).

Reflection Mid-FTIR. In order to establish whether or not it is possible to detect the differences between the various chrome yellow forms in a noninvasive manner on paintings, all paint models were examined also by reflection mid-FTIR. A comparison of Figure 2B to 2A illustrates the presence of spectral distortions. These anomalies depend on the band strength, concentration, particle size distribution, and the setup geometry.
Raman Spectroscopy. Figure 2C shows Raman spectra of the model paints obtained by the benchtop device (black lines). Details about the mathematical treatment of spectra are reported in Figure S-3 of the Supporting Information. (Data obtained from D1 and D2 give results similar to those of S3C and S1mono and are therefore not shown.)

When the sulfate amount increases, the wavenumber of the \( \nu_1(\text{CrO}_4^{2-}) \) stretching mode monotonically increases from 841 cm\(^{-1} \) to 844 cm\(^{-1} \) for PbCrO\(_4\) (S1mono and Sortho) to 844 cm\(^{-1} \) for S1ortho and S3D (Figures 2C and S-3A of the Supporting Information). Consistent with the literature, \( \nu_1(\text{CrO}_4^{2-}) \) modes are located at 400, 376, and 357 cm\(^{-1} \), while those at 336 and 323 cm\(^{-1} \) are attributable to the \( \nu_2(\text{CrO}_4^{2-}) \) vibration. The band between 339 and 342 cm\(^{-1} \) is characteristic for the presence of orthorhombic compounds, becoming clearly visible for S1ortho and Sortho (Figures 2C and S-3B). Similar to the chromate vibrations, the \( \nu_1(\text{SO}_4^{2-}) \) position shifts from 971 cm\(^{-1} \) (S1ortho) to 980 cm\(^{-1} \) (D2p, the pure PbSO\(_4\)) (Figure 2C).

As done for FTIR spectroscopy, equivalent data were collected by a portable Raman spectrometer suitable for in situ analyses. Figure 2C (red lines) illustrates that, despite the lower instrumental spectral resolution, analogous systematic differences can be observed as a function of the \( \text{CrO}_4^{2-}:\text{SO}_4^{2-} \) ratio.

Identification of Different Forms of Chrome Yellow Pigments in Historic Paint-tube Samples and Microsamples of Original Paintings. Table 2 reports a list of 22 paint samples obtained from a series of 12 paintings by Van Gogh, one Gauguin painting, the palette by Van Gogh and Cézanne, and 5 historic oil-paint tubes. In 20 cases, XRD, reference paints S1mono, S1ortho, S3C, and PbSO\(_4\) (Figure S-3A of the Supporting Information). Consistent with the literature, \( \nu_1(\text{CrO}_4^{2-}) \) for S1ortho and Sortho to 844 cm\(^{-1} \) for S1ortho and S3D (Figures 2C and S-3A). Similar to the chromate vibrations, the \( \nu_1(\text{SO}_4^{2-}) \) position shifts from 971 cm\(^{-1} \) (S1ortho) to 980 cm\(^{-1} \) (D2p, the pure PbSO\(_4\)) (Figure 2C).

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Historical Chrome Yellow Paints. In order to characterize the historic chrome yellow paints A, B1, B2, DG1, and DG2, the spectral features are analogous to that of monoclinic co-precipitate S1b for DG1, the vibrational spectral features are analogous to that of 866 monoclinic PbCrO\(_4\) (cf. Table 1 and Figures 2A and 2C). Transmission mid-FTIR (Figure 3B) and Raman spectra (Figure 3C) of sample A show features that are mostly similar to the materials having an orthorhombic phase (S1ortho/D2, Sortho), while the spectra of the other (less S-rich) paint samples B1, B2, and DG resemble that of monoclinic co-precipitate S1b; for DG2, the vibrational spectral features are analogous to that of 866 monoclinic PbCrO\(_4\) (cf. Table 1 and Figures 2A and 2C). These observations are confirmed by XRD (Figure 3A).

In the FTIR spectra of B1 and B2, the \( \nu_2(\text{CrO}_4^{2-}) \) and \( \nu_2(\text{SO}_4^{2-}) \) band shapes show differences due to the presence of MgCO\(_3\), which contributes with signals around 800 and 597 cm\(^{-1} \) while for DG2, B1, and B2 (dark chrome yellow), additional Raman bands at 826, 376, 372, 340, and 323 cm\(^{-1} \) are ascribable to phoenicochrome, a compound also identified by XRD.

The above-mentioned results point to the fact that the historic chrome yellow paint A, a material that proved itself to be very susceptible to 866 darkening due to UVA-visible irradiation, contains orthorhombic PbCr\(_{1-x}\)S\(_{x}\)O\(_4\) phases, while the materials that proved to be significantly less prone to darkening (B1 and B2)3 contain the reference paints S1mono, S1ortho, S3C, and PbSO\(_4\). A small amount of monoclinic PbCr\(_{1-x}\)S\(_{x}\)O\(_4\) is also likely to be present. For this paint, Figure 3A illustrates that comparable XRD patterns were obtained by SR-based, benchtop, and, despite the lower spectral resolution, portable instrumentation.

HAADF/STEM-EDX and S K-edge XANES analyses of paint A (Figure S-5A/B of the Supporting Information) confirm the presence of the orthorhombic co-precipitate as in XRD. Transmission mid-FTIR (Figure 3B) and Raman spectra (Figure 3C) of sample A show features that are mostly similar to the materials having an orthorhombic phase (S1ortho/D2, Sortho), while the spectra of the other (less S-rich) paint samples B1, B2, and DG resemble that of monoclinic co-precipitate S1b; for DG2, the vibrational spectral features are analogous to that of 866 monoclinic PbCrO\(_4\) (cf. Table 1 and Figures 2A and 2C). These observations are confirmed by XRD (Figure 3A).

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The above-mentioned results point to the fact that the historic chrome yellow paint A, a material that proved itself to be very susceptible to 866 darkening due to UVA-visible irradiation, contains orthorhombic PbCr\(_{1-x}\)S\(_{x}\)O\(_4\) phases, while the materials that proved to be significantly less prone to darkening (B1 and B2)3 contain the monoclinic ones.

Embedded Paint Microsamples and Noninvasive in Situ Investigations. Investigations of the yellow areas of embedded paint microsamples F409/1, 10872, F603/3, 10455, 224/1, and F816/3 (Figure 4A) clearly demonstrate the presence of different chrome yellow forms (see also Table 2). FTIR (Figure 4B) and Raman (Figure 4C) spectra, compared to those of the reference paints S1ortho, S1b, and S1c, show that the yellow-orange paint layer of F409/1 and 10872 is composed of monoclinic PbCrO\(_4\) while the lighter-yellow regions of the other ones are formed by PbCr\(_{1-x}\)S\(_{x}\)O\(_4\). More in depth, it appears that for F603/3 and 10455, the PbCr\(_{1-x}\)S\(_{x}\)O\(_4\) composition is close to that of the S1b model in which the monoclinic structure dominates, while for F816/3 and 224/1, the spectral features resemble those of S1c containing both the monoclinic and the orthorhombic form. These vibrational spectroscopic results were also confirmed.
by the SR μ-XRD measurements (not shown in Figure 4, cf. Figure 1A). Although the μ-FTIR, Raman, and SR μ-XRD analyses clearly demonstrated only the presence of S-rich monoclinic PbCr$_{1-x}$S$_x$O$_4$ in F816/3 and 224/1, the additional presence of very low quantities of the orthorhombic phase cannot be excluded for these samples, since a coexistence of both monoclinic and orthorhombic PbCr$_{1-x}$S$_x$O$_4$ can be observed starting from an SO$_4^{2-}$ molar amount of around 40%.13

Figure 3. (A) XRD, (B) transmission mid-FTIR, and (C) Raman spectral data of the historic chrome yellow paints DG$_1$, DG$_2$, B$_1$, B$_2$, and A. In (A), the XRD pattern of sample A collected by the benchtop (black), portable (red), and SR-based (blue) device are shown. In gray, spectra of reference S$_{\text{mono}}$ and S$_{\text{b}}$; P labels indicate the peaks of phoenicochroite.

Figure 4. From top to bottom: (A) optical microscope images, (B) reflection mid-FTIR, and (C) Raman spectra collected from yellow areas of the original embedded paint microsamples F816/3, 224/1, 10455, F603/3, 10872, and F409/1 taken from different Van Gogh paintings (see Table 2 for further details). In (B) and (C), spectra of paints S$_{\text{mono}}$, S$_{\text{b}}$, and S$_{\text{c}}$ are illustrated in red color.
Finally, in order to ascertain whether or not it is possible to distinguish among different forms of PbCr\(_1\)S\(_2\)O\(_4\) via non-invasive in situ measurements, we have examined Van Gogh’s Portrait of Gauguin (Figure 5A) at the Van Gogh Museum using the combined use of analytical techniques such as XRD, FTIR, and Raman spectroscopy and SR-based methods such as SR-μ-XRD and S K-edge μ-XANES. Preliminary in situ reflection mid-FTIR investigations performed on yellow areas of the painting, Portrait of Gauguin by Van Gogh, allowed us to identify the presence of PbCr\(_1\)S\(_2\)O\(_4\) and mixtures of monoclinic and orthorhombic PbCr\(_1\)S\(_2\)O\(_4\) was demonstrated. A co-precipitated PbCr\(_1\)S\(_2\)O\(_4\) form was also found in one painting by Gauguin and in one sample from a palette used by Cézanne.

A relevant result is that the characterization of different chrome yellow forms is possible by using portable instrumentation. Preliminary in situ reflection mid-FTIR investigations performed on yellow areas of the painting, Portrait of Gauguin by Van Gogh, allowed us to identify the presence of PbCr\(_1\)S\(_2\)O\(_4\) chrome yellow composed of a mixture of monoclinic and orthorhombic phases. This result was confirmed by laboratory measurements on a related microsample.

As described in the following paper (part 4), the relation between the sulfate content, the crystal form, and the susceptibility to darkening during photochemical aging of different chrome yellow-based model paints has been investigated. The results demonstrate that the exact nature of the chrome yellow type strongly influences its long-term stability.

For this reason, future work will be dedicated to a detailed study by SR-μ-XANES and μ-XRF investigations of a selection of the microsamples of Table 2, with the aim of exploring whether or not it is possible to establish an effective correlation between the chrome yellow composition/crystalline structure and the state of preservation of the pigment in original paintings. On the other hand, we will also seek to more systematically document the relation between the occurrence of the different types of chrome yellow and their exact hue/context/function in Van Gogh’s work.

Figure 5. (A) Photographs of Portrait of Gauguin (37 × 33 cm, F546 s257v/1962) by Vincent van Gogh (1888, Van Gogh Museum, Amsterdam, The Netherlands) and a related microsample, X448_2. (B) Reflection mid-FTIR spectra recorded from the yellow lacunae (blue) and the outer pale yellow areas (black). (C) Raman spectrum (black) obtained from the yellow region of X448_2. In (A), labels indicate areas where FTIR data were acquired, while the dotted yellow rectangle points out the sampling location; LW shows the (B) bending and (C) stretching modes of CO\(_3\)^\(^2\)- group of lead white. In (B and C) (red) spectra of paints S\(_{\text{SB}}\) and S\(_{\text{SC}}\).
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