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The examination of Van Gogh's chrome yellow pigments in 'Field with Irises near Arles' using quantitative SEM–WDX

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Abstract

In this paper we present the results of quantitative measurements on the pigment chrome yellow ($PbCr_{1-x}S_xO_4$ with $0 \leq x \leq 0.8$) using scanning electron microscopy-wavelength dispersive X-ray analysis (SEM–WDX). Traditionally, Optical Microscopy (OM) in combination with scanning electron microscopy-energy dispersive X-ray analysis (SEM–EDX) is used for the identification of many pigments in paint cross-sections based on their particle characteristics and elemental composition. However, in the case of chrome yellow, the lead (Pb) and sulphur (S) peaks overlap, which makes quantitative analysis unreliable. SEM–WDX does not suffer from this problem and we have demonstrated that this technique can distinguish different types of chrome yellow based on the quantification of the sulphur-content of the pigment. This identification can be performed on paint cross-sections, allowing for distinction between chrome yellows in different paint layers. In addition, our study showed that the different types of chrome yellow can still be identified even in low concentrations. Van Gogh made wide use of different hues of chrome yellow. Using this method, we have identified the types of chrome yellow he used in *Field with Irises near Arles*, which we have been able to correlate with the information in his letters. Raman spectroscopy of the same samples confirmed the SEM–WDX results, but evidenced a higher sensitivity of the latter technique in revealing small amounts of sulphur-rich $PbCr_{1-x}S_xO_4$ in mixtures with $PbCrO_4$. SEM–WDX is also more accurate, because it allows the lead(II) sulphate fraction to be determined within 1 mol% absolute, whereas with Raman spectroscopy only relatively broad ranges can be defined. The on-going research of Van Gogh's paintings as part of a cataloguing project—a collaboration between the Van Gogh Museum, the Cultural Heritage Agency of the Netherlands and Shell—opens the way for a comprehensive comparison of the chrome yellows used by Van Gogh using SEM–WDX.

Keywords: SEM, EDX, WDX, Raman, Van Gogh, Pigments, Chrome yellow

Introduction

Chrome yellow pigments were invented in the early nineteenth century, with hues ranging from lemon-yellow to deep orange-yellow depending on the composition and crystal structure of the pigment [1, 2]. Chrome yellow can be denoted with the general formula $PbCr_{1-x}S_xO_4$ ($0 \leq x \leq 0.8$). Chrome yellows that do not contain any sulphate ($x = 0$) are medium yellow in colour and have a monoclinic crystal structure, while the more orange-yellow varieties contain some chrome orange (Pb_2CrO_5) in addition [3]. The lighter varieties show variable amounts of sulphate and might exist in both the monoclinic and orthorhombic crystal structure, the latter becoming favorable when higher amounts of sulphate are present [4].

Van Gogh made use of these different hues of chrome yellow. His letters to his brother Theo include lists of paints that he wanted his brother to buy on his behalf. In these paint orders, he requests three different hues of chrome yellow: Chrome 1, Chrome 2 and Chrome 3, described as the lemon, the yellow and the orange.[1]

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[1] Letter 595, from Vincent van Gogh to Theo van Gogh, Arles, on or about Wednesday, 11 April 1888.

Fig. 1 Vincent van Gogh, *Field with Irises near Arles* (F409), 1888, Van Gogh Museum, Amsterdam (Vincent van Gogh Foundation). Locations where the samples were taken are indicated. For samples F409/2, 3 and 7a there are no records of the sampling locations; therefore, it is only possible to determine a likely area in the painting from which the samples were taken based on the paint layer structure and composition

Chemical analysis of paint samples has, indeed, shown the presence of different types of chrome yellow in his paintings [5, 6].

Field with Irises near Arles (F409) was painted by Van Gogh in May 1888, just a few months after his arrival in Arles in February 1888 (Fig. 1). He had probably brought some paints with him from Paris, where he had lived before he came to Arles, but started to look for a good local supplier soon after his arrival. When he failed to find one to his satisfaction, he decided to order his paints from his former dealers Tasset et L'Hôte and Tanguy via his brother Theo in Paris. He placed his first order for paints, including the three types of chrome yellow mentioned above, in a letter of 5 April 1888,[2] which he received from Tasset et L'Hôte soon afterwards.[3]

It is known from literature that chrome yellow oil paint is prone to darkening or browning due to photo-reduction of the chromate ions to chromium(III)-compounds. This concerns especially the sulphate-rich, orthorhombic variety of the pigment; the monoclinic lead chromate variety appears to be much more lightfast [1, 7–9], although Otero et al. have demonstrated that the presence of calcium carbonate and/or gypsum—materials often encountered in Van Gogh's chrome yellow paints [10, 11]—in chrome yellow oil paint enhances the reactivity of the latter variety [12]. Indeed, paints containing this supposed more stable variety are often in a deteriorated and vulnerable condition and show darkening as well. In *Field with Irises near Arles*, the colour change of the assumed pure lead chromate paint is probably caused by external influences—like deposition of material on the surface—rather than deterioration of the pigment itself [13, 14].

The Van Gogh Museum, the Cultural Heritage Agency of the Netherlands and Shell collaborated in several projects on the painting materials and techniques of Van

[2] Letter 593, from Vincent van Gogh to Theo van Gogh. Arles, on or about Thursday, 5 April 1888.

[3] Letter 595, from Vincent van Gogh to Theo van Gogh, Arles, on or about Wednesday, 11 April 1888.

Gogh. Currently, approximately eighty paintings that Van Gogh painted in Arles, Saint-Rémy-de-Provence and Auvers-sur-Oise (1888–1890) are being examined in the Van Gogh Museum as part of a cataloguing project performed by these research partners. In these projects hundreds of paint cross-sections have been examined, mostly using optical microscopy and scanning electron microscopy (SEM) in combination with energy dispersive X-ray analysis (EDX) [10, 11]. This technique is widely used to study paint samples from works of art and provides reliable qualitative and semi-quantitative compositional results [15–18]. It does, however, have some limitations, particularly regarding overlapping peaks due to its relatively low energy resolution. In the case of chrome yellow, optical microscopy in combination with SEM–EDX can provide an indication of the type of chrome yellow used based on the morphology and hue of the chrome yellow pigment, but it does not allow for proper identification of the variety of chrome yellow, since Pb-Mα and S-Kα lines overlap in the SEM–EDX spectrum. In order to distinguish between the different types of chrome yellow, additional analysis is needed. X-ray diffraction (XRD) is most commonly applied to identify these crystalline compounds [19]. This technique generally requires a loose paint sample, but synchrotron based XRD has successfully been applied on paint cross-sections [6]. Alternatively, Fourier Transform Infrared Spectroscopy (FTIR) or Raman-analysis can be used to differentiate between the types of chrome yellow used in a painting [6–8]. Also, the development of non-invasive, in situ XRD and Raman analysis have made it possible to differentiate between types of chrome yellow without sampling [20–22], but these techniques are not very widespread.

One way to overcome the limitation of SEM–EDX regarding overlapping peaks is to use Wavelength Dispersive X-ray analysis (WDX), which is known to have a much higher energy resolution than SEM–EDX. In the field of conservation this technique has been used to study ancient glass and glazes in ceramics [23–26], but only sporadically in the research of historic paints [27]. In this paper we explore the application of SEM–WDX on paint cross-sections taken from *Field with Irises near Arles*. Because of its higher energy resolution it should resolve the overlap issue between lead and sulphur, which would allow for the distinction of different varieties of chrome yellow. Micro-Raman spectroscopy was used for comparison and validation of the SEM–WDX results.

Experimental

Standards

To determine how accurately SEM–WDX can measure the composition of chrome yellow, two types of standards were prepared, namely: known mixtures of lead(II) sulphate and lead(II) chromate in order to test how accurately the lead to sulphur ratio could be determined; and mixtures of lead(II) chromate sulphate ($PbCr_{0.5}S_{0.5}O_4$) in lead white, which were used to test to what extent it was possible to still measure the chrome yellow composition when the pigment has been mixed with lead white.

The standards were prepared as follows: for the determination of the lead to sulphur ratio lead(II) sulphate 98% (Aldrich) and lead(II) chromate ≥ 98% (Aldrich) were weighed and mixed thoroughly in a mortar, resulting in 5, 14, 27, 49 and 77 mol% mixtures of lead(II) sulphate to lead(II) chromate. For the determination of sulphate-rich chrome yellow in lead white, primrose chrome yellow was used. This was prepared by Vanessa Otero (Universidade NOVA de Lisboa) according to the Winsor and Newton manufacturing process (Pr1b_2, corresponding to $PbCr_{0.5}S_{0.5}O_4$) [3, 28]. Mixtures of 0.1, 0.9, 4 and 10 wt% of the Pr1b_2 chrome yellow pigment were mixed with lead white, basic lead carbonate ($2PbCO_3{\cdot}Pb(OH)_2$, ca. 99%, Kremer pigment), in a mortar. The mixtures, as well as the unmixed lead(II) sulphate, lead(II) chromate and lead(II) chromate sulphate (Pr1b_2 pigment), were embedded in Polypol PS230 polyester resin cubes and polished with SiC-paper (Struers and Micromesh).

Paint samples taken from Field with Irises near Arles

Paint samples were taken from *Field with Irises near Arles* around 1930 by the conservator and scientist Martin de Wild. Subsequently, they were kept in plastic pots. The sampling locations of these samples are unknown. In addition, four new samples were taken from the painting during a recent conservation treatment. All samples were embedded in a Polypol PS230 polyester resin cube and a polished cross-section was prepared using SiC-paper (Struers and Micromesh). The resulting paint cross-sections were examined using a Zeiss Axioplan 2 optical microscope both with incident polarised light and incident UV-light (from a Xenon-lamp and a mercury short arc photo optic lamp HBO, respectively). Subsequently, they were analyzed with SEM–EDX using a JEOL JSM 6490 LV scanning electron microscope and a Noran System Six EDS-system. The primary electron beam energy used was 25 keV. The cross-sections were coated with carbon and examined in high vacuum mode. These analyses showed the presence of chrome yellow in three of the samples taken by De Wild (samples F409/2, 3 and 7a) as well as in one sample that was recently taken from one of the irises along the bottom edge of the painting (sample F409/6). This sample contains both the red paint from the iris plus some yellow-green paint from the field (Fig. 2).

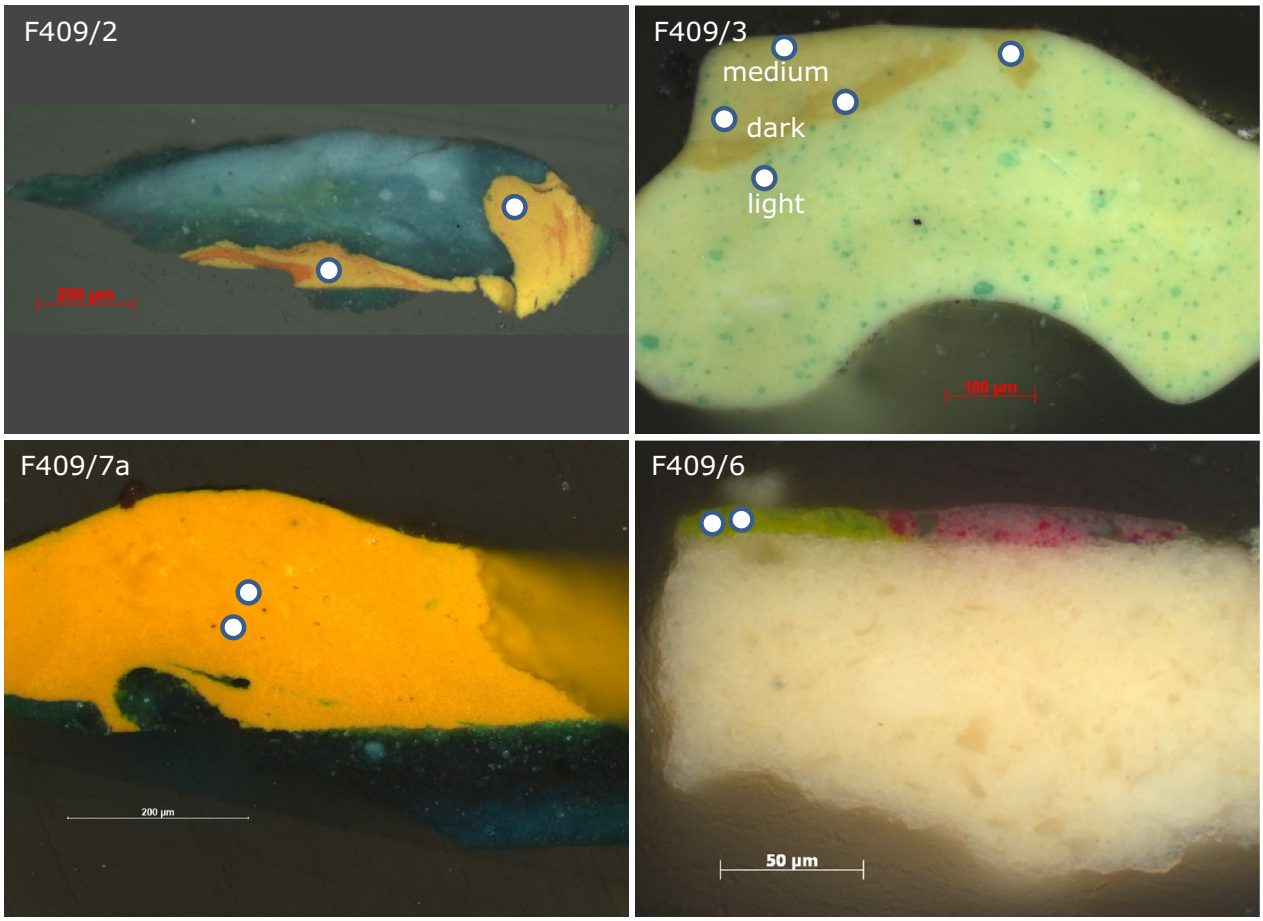

Fig. 2 Cross-sections of paint samples taken from *Field with Irises near Arles*. White dots indicate the approximate locations of the WDX-analyses. The Raman spectra were collected in the same areas

SEM–WDX analysis

To reduce charging in the SEM, the samples were coated with carbon. The samples were examined with an Oxford Wave WDX system mounted on a Zeiss EVO60 XVP SEM. All images were made using backscattered electrons. Typically, three spectra were taken from different points in each sample using an accelerating voltage of 20 kV. When selecting the regions to be measured, care was taken to only select yellow areas (visualised on images taken using OM), thus avoiding any contributions to the chromium and sulphur signal from other pigments, such as viridian (transparent chromium oxide green), chrome orange (basic lead chromate) or synthetic ultramarine blue (a complex aluminium and sulphur-containing sodium-silicate). A magnification was chosen so that as much of the sample as possible could be measured which was typically around 1000 times. As a final check, prior to the WDX measurement, the selected area was also measured using EDX (Oxford X-max EDS-system with a 20 keV primary electron beam energy) to confirm that the area contained no unwanted pigments or fillers, such as calcium or barium sulphate. The beam current used for the WDX measurements was typically between 10 and 15 nA and the measuring time per peak varied from 5 to 20 s. The beam current chosen is larger than is typically used for SEM–EDX, but was needed in order to measure the spectra in a reasonable time and thus avoid experimental artefacts that might arise due to, for example, sample and beam current drift. The WDX peak height was used for the quantification with the background subtracted. After SEM–WDX analysis the carbon coating was removed by polishing and the paint cross-sections were re-examined by OM. No damage of the paint cross-sections was visible under these circumstances.

Micro-Raman spectroscopy

The micro-Raman spectra were obtained with a Perkin-Elmer Raman Micro 300 (Raman microscope) and a Raman Station 400F (Raman spectrometer) with a

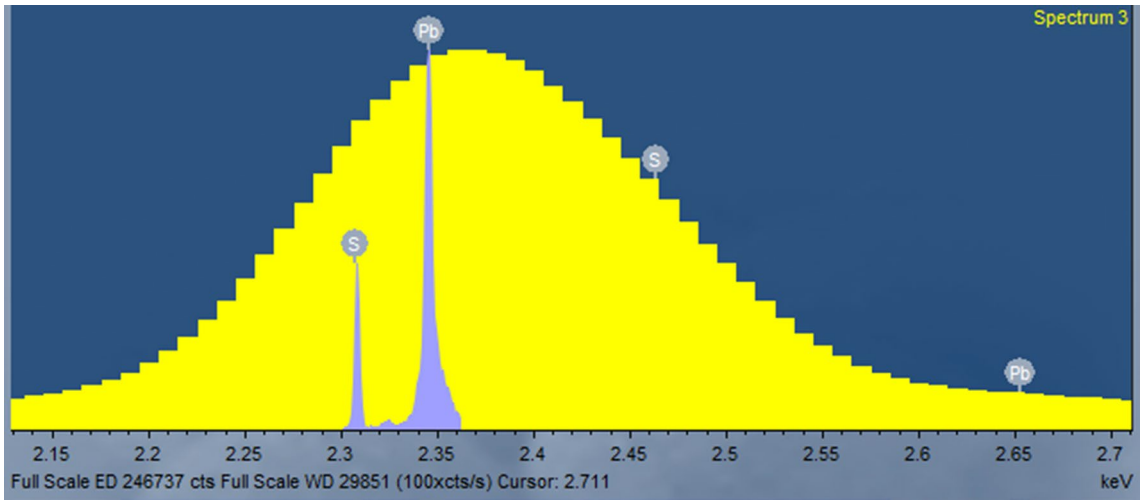

Fig. 3 Comparison of the EDX and WDX spectra from the same region of the 49 mol% lead(II) sulphate to lead chromate standard (yellow is EDX, purple is WDX)

diode laser ($\lambda_0 = 785$ nm), in combination with a Olympus BX51M microscope. Exposure time, laser power and accumulations were selected for each measurement to obtain optimal spectra. The laser spot has a diameter of ca. 20 µm (50× objective) or 10 µm (100× objective) and the laser power (10–100%) varies in the range of 7–70 mW (50× objective) and 4–40 mW (100× objective) with a 600 lines/mm grating. Raman scattering is filtered with a double holographic notch filter system and is detected with an air-cooled charge coupled device (CCD) detector. The Raman spectra were processed with Origin 8.0 software.

Results and discussion

SEM–WDX has a resolution of around 10 eV compared to around 130 eV for EDX. The difference this makes becomes apparent when the EDX and WDX spectra from the same region of the 49% lead(II) sulphate to lead chromate standard are shown overlaid (Fig. 3). The sulphur peak is clearly visible in the WDX spectrum, but not in the EDX measurement. This illustrates one of the main advantages of WDX over EDX in that it can clearly measure both the lead and sulphur peaks and thus unambiguously confirm the presence of both elements. This is not the case in EDX. Although peak fitting routines can be employed to determine the amount of sulphur and lead, this can lead to greater uncertainty, especially when the concentration of sulphur is low. As WDX does not suffer from any peak overlap, the limit of detection is simply related to the sensitivity of the WDX detector itself.

To test the sensitivity of the WDX detector, a series of standards which contained known amounts of lead(II) sulphate and lead(II) chromate were measured: the results are shown in Fig. 4. Examination of these results reveals a positive, linear correlation between the amount of lead(II) sulphate and the sulphur signal measured with WDX. We used these results to determine a conversion factor to convert the sulphur measured with the WDX into the fraction of lead(II) sulphate. This was done by using a linear extrapolation of the data in Fig. 4 with the intercept set to zero. The R^2 value was 0.9886, which suggests that this gives a reliable fit.

To test the detection limit of WDX, we measured a series of standards where primrose chrome yellow pigment was mixed with lead white. The pure primrose chrome yellow pigment contained around 50 mol% lead(II) sulphate (hence $PbCr_{0.5}S_{0.5}O_4$) as determined by WDX. This is in good agreement with results from FTIR- and Raman-measurements in literature [28] and performed in our laboratory. All spectral features of $PbCr_{0.5}S_{0.5}O_4$ [5, 14] could be clearly observed: the Raman signals of the $\nu_1(SO_4^{2-})$ mode at 973 cm^{-1}, the $\nu_1(CrO_4^{2-})$ mode at 843 cm^{-1} and the five modes in the Cr–O bending region at 405, 377, 358, and 337, 325 cm^{-1}. With WDX the sulphur from the standards containing more than 5 wt% of the lead chromate sulphate pigment could be detected, as defined by the height of the sulphur peak being at least three times the background signal. This suggests that the detection limit for this WDX method is around this level.

The same standards—where different amounts of primrose chrome yellow pigment were mixed with lead white—were also analysed with micro-Raman spectroscopy (data not shown). The distinctive features for

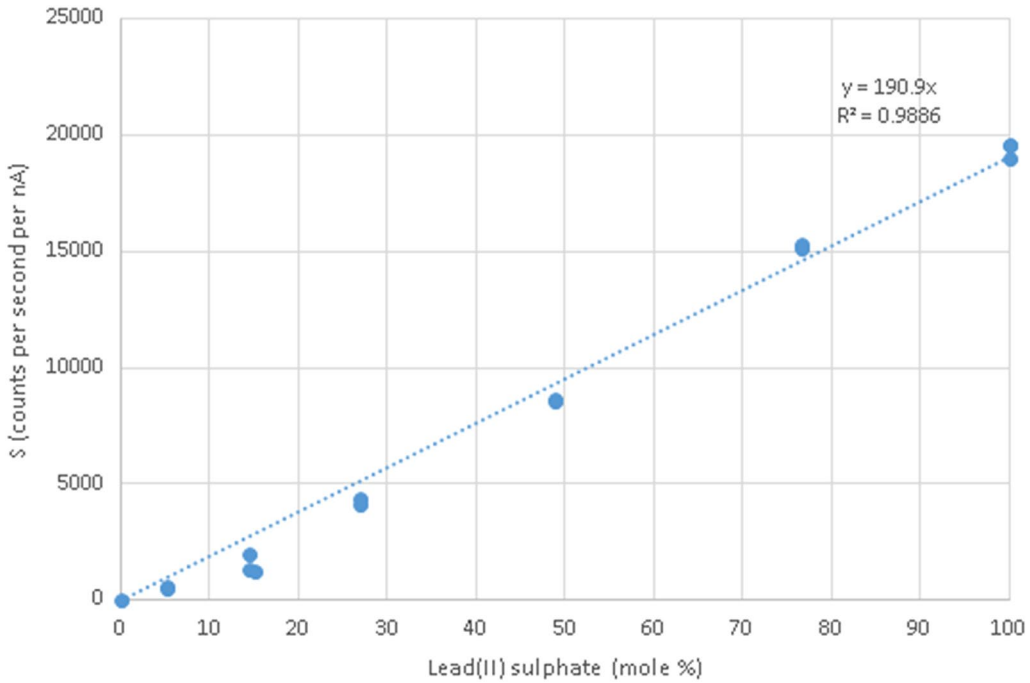

Fig. 4 Plot of the amount of lead(II) sulphate versus the sulphur signal measured using WDX in the lead(II) sulphate and lead(II) chromate mixtures standards

$PbCr_{0.5}S_{0.5}O_4$ could still be observed for the 5 wt% of the lead chromate sulphate pigment. At lower concentrations (1 wt% and 0.1 wt%) the characteristic peaks in the Cr–O bending region are very low and broad. So, comparable detection limits as with WDX were obtained.

To determine the amount of lead(II) sulphate in the chrome yellow pigment we used the ratio of the sulphur signal to the sum of the chromium and sulphur signals. Figure 5 shows the results of this ratio from the measurements of the 27, 49 and 77 mol% mixtures standards of lead(II) sulphate to lead(II) chromate as well as of the unmixed lead(II) sulphate and lead(II) chromate. From these data, a conversion factor was also determined using linear extrapolation with the intercept set to zero. The R^2 value was 0.9818. Although this is not as good as the lead versus sulphur plot, as this is lead independent, it is our preferred method of determining the lead(II) sulphate fraction in chrome yellow. To test the accuracy of the conversion factor two additional standards with 14 mol% and 5 mol% lead(II) sulphate mixed with lead(II) chromate were analysed. For the 14 mol% nominal standard 14.0 was measured with a 95% confidence of ± 0.58; the expected value was 14.4. For the 5 mol% nominal standard 5.1 was measured with a 95% confidence of ± 0.51; the expected value was 5.1. One sample t-tests showed that the measured value is not significantly different from the expected value at an alpha of 0.05 for both standards. These results indicate that the WDX can determine the lead(II) sulphate fraction to within approximately 1 mol% absolute.

The results from the measurements on the various standards show that we can use WDX to determine the fraction of lead(II) sulphate in both pure chrome yellow pigment as well as in mixtures of this pigment in lead white. This now makes it possible to determine the fraction of lead(II) sulphate in chrome yellow in paint samples from actual paintings. As an example, we have measured the composition of chrome yellow containing paint samples taken from Van Gogh's *Field with Irises near Arles*. A summary of the results of the SEM–WDX analysis and micro-Raman spectroscopy of these samples is shown in Table 1.

Both paint cross-sections F409/2 and F409/7a taken by De Wild have a similar layer build-up: paint layers of emerald green, Prussian blue and lead white in different ratios below and—in case of F409/2—also on top of the chrome yellow paint layer (Fig. 2). These colours and build-up of paint layers resemble the way Van Gogh painted the field, as established when the paint surface was examined using an optical microscope. Therefore, the samples might have been taken from the (ochreish) yellow buttercups in the foreground of the painting.

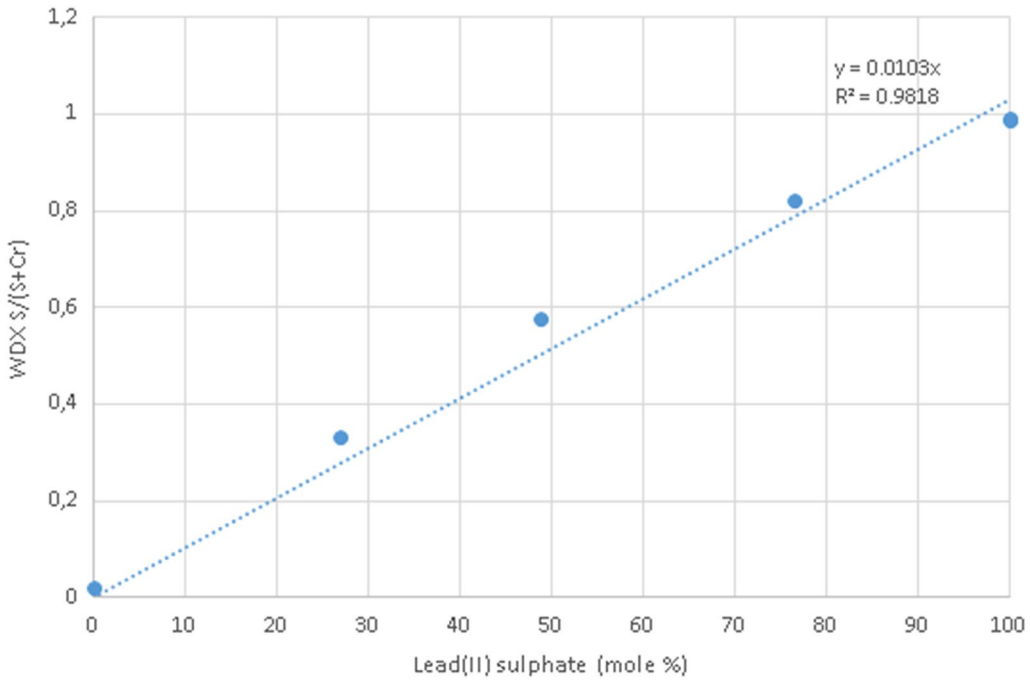

Fig. 5 Plot of the amount of lead(II) sulphate versus the ratio of sulphur to the sum of the chromium and sulphur measured using WDX in the lead(II) sulphate and lead(II) chromate mixtures standards

Table 1 Summary of the SEM–WDX and Raman results of chrome yellow containing paint samples taken from *Field with Irises near Arles*

Sample ID	(Probable) location	SEM–WDX estimated fraction of lead(II) sulphate in chrome yellow (mol%)	Raman estimated fraction of lead (II) sulphate in chrome yellow (mol%)[a]
F409/2	Brown yellow buttercups in foreground	6	0
F409/3 dark yellow	Yellow paint from the field in the background	50	50
F409/3 medium yellow	Yellow paint from the field in the background	51	50
F409/3 light yellow	Yellow paint from the field in the background	51	50
F409/6	Yellow green paint from the field	24–42	25–50[b]
F409/7a	Brown yellow buttercups in foreground	5	0

[a] Estimation based on the method described by Monico et al. [20]

[b] The signals in the Raman spectrum are very weak so peak assignments are uncertain

The chrome yellow paints in both cross-sections contain calcium carbonate, which was probably added by the paint manufacturer in order to obtain a lighter shade or to enhance the working properties of the paint, although it can also form as a by-product in the production of chrome yellow under certain conditions [29]. Interestingly, Otero et al. reported in their study on Winsor and Newton's production records that the presence of calcium carbonate is characteristic of their middle chrome formulations [3]. The yellow paint layer in F409/2 is inhomogeneously mixed with the orange-red pigment red lead; these reddish areas were avoided in our measurements.

Examination of the SEM–WDX results shown in Table 1 reveals that the yellow paint layers in cross-sections F409/2 and F409/7a contain the same type of

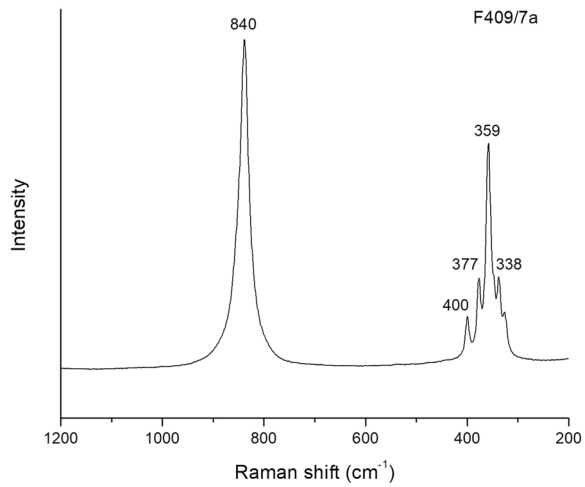

Fig. 6 Raman spectrum collected from the yellow paint layer of cross section F409/7a

chrome yellow pigment: the fraction of lead(II) sulphate being very low, around 5–6 mol%. This type of chrome yellow probably corresponds to a medium colored variant of the pigment, generally assumed to contain mainly lead(II) chromate ($PbCrO_4$), with small amounts of lead(II) chromate sulphate [1]. Monico et al. [6] identified monoclinic lead(II) chromate in another sample taken from *Field with Irises near Arles*. In our study micro-Raman spectroscopy was also used to analyse the yellow paint of samples F409/2 and F409/7a (Fig. 6). Similar spectra were obtained with main peaks at 840 cm^{-1} and at 400, 377, 359, and 338 cm^{-1}. No $\nu_1(SO_4^{2-})$ mode could be detected, suggesting that the relative amount of sulphate is low. These results indicate the presence of monoclinic $PbCrO_4$ alone or, as suggested by the SEM–WDX results, in a mixture with very small amounts of lead(II) chromate sulphate. According to Monico et al. [20], it is difficult to detect small amounts of sulphur-rich $PbCr_{1-x}S_xO_4$ if mixed with relatively high amounts of monoclinic $PbCrO_4$. In this study the superior sensitivity of SEM–WDX was capable of detecting 5–6 mol% of sulphate.

Cross-section F409/3 consists of three paint layers containing chrome yellow mixed with lead white and, in addition, some emerald green in the bottom and top layer (Fig. 2). This paint sample was possibly taken from the yellow paint in the field in the background. The bottom paint layer is the lightest in colour, followed by a darker yellow layer and, finally, a medium yellow layer. SEM–WDX analysis showed that in all three layers the chrome yellow is of the same sulphur-rich type with a fraction of approximately 50% of lead(II) sulphate. The differences in hue of the yellow layers was in this case accomplished by varying the amount of lead white, and is not related to the type of chrome yellow used. The chrome yellow present in this cross-section differs from the one identified in F409/2 and F409/7a. It corresponds to a lighter variety of the pigment, probably sold as primrose or lemon yellow.

Raman measurements of cross section F409/3 show that the yellow pigments in the three layers yield similar spectra with bands at 972, 842/843, 404/405, 377, 360, and 338 cm^{-1} (Fig. 7). The same spectral features were observed for the pure primrose chrome yellow pigment and indicate the presence of monoclinic $PbCr_{1-x}S_xO_4$ with $x \sim 0.5$. This seems to be confirmed by the absence of signals at 450 and 438 cm^{-1} (sulphate bending modes), suggesting a S-rich coprecipitate with $x < 0.75$ [20]. As expected, the relative amount of lead white (1049 cm^{-1}) is highest in the light yellow and lowest in the dark yellow paint layers. In the medium yellow layer some chrome orange is also present, as indicated by the shoulder at 826 cm^{-1}. A mixture of chrome orange and $PbCr_{1-x}S_xO_4$ with $x > 0.4$ was also found in two regions of the sunflower petals with an orange-yellow tone in the *Sunflowers* owned by the Van Gogh Museum [30].

The cross-section from a sample taken from one of the irises (F409/6) in the foreground includes the yellow-green paint of the vegetation (Fig. 2). This paint contains a mixture of the pigments emerald green and chrome yellow and the fillers barium sulphate and calcium carbonate. The presence of the sulphur from barium sulphate complicates the analysis of the chrome yellow. In order to correct for the sulphur from the barium sulphate, we used the barium to sulphur ratio from a barium sulphate crystal in the layer and then used the barium signal from the regions of interest to estimate the associated sulphur signal. This signal was then subtracted from the overall signal in order to give the amount of sulphur associated with the chrome yellow. In practice, we have found that the barium to sulphur ratio varies significantly, both within one crystal as well as between different crystals. This is probably due to the small size of the crystals, which means that there is a contribution from the surrounding region. As a result, it is not possible, at present, to give an absolute value. Instead, we estimated the fraction of lead(II) sulphate in the chrome yellow as being in the range 24 to 42 mol%. This would suggest that Van Gogh used yet another variety of chrome yellow in *Field with Irises near Arles,* which has a hue in between lemon and medium yellow. However, it could also be possible that Van Gogh mixed the two varieties of chrome yellow [31].[4]

[4] It is clear from his letters that Van Gogh did sometimes mix his chrome yellow paints. In a letter to Emile Bernard written on or about Tuesday 19 June 1888 in Arles he e.g. describes The Sower (F422): "The chrome yellow 1 sky almost as bright as the sun itself, which is chrome yellow 1 with a little white, while the rest of the sky is chrome yellow 1 and 2 mixed, very yellow, then." (www.vangoghletters.org).

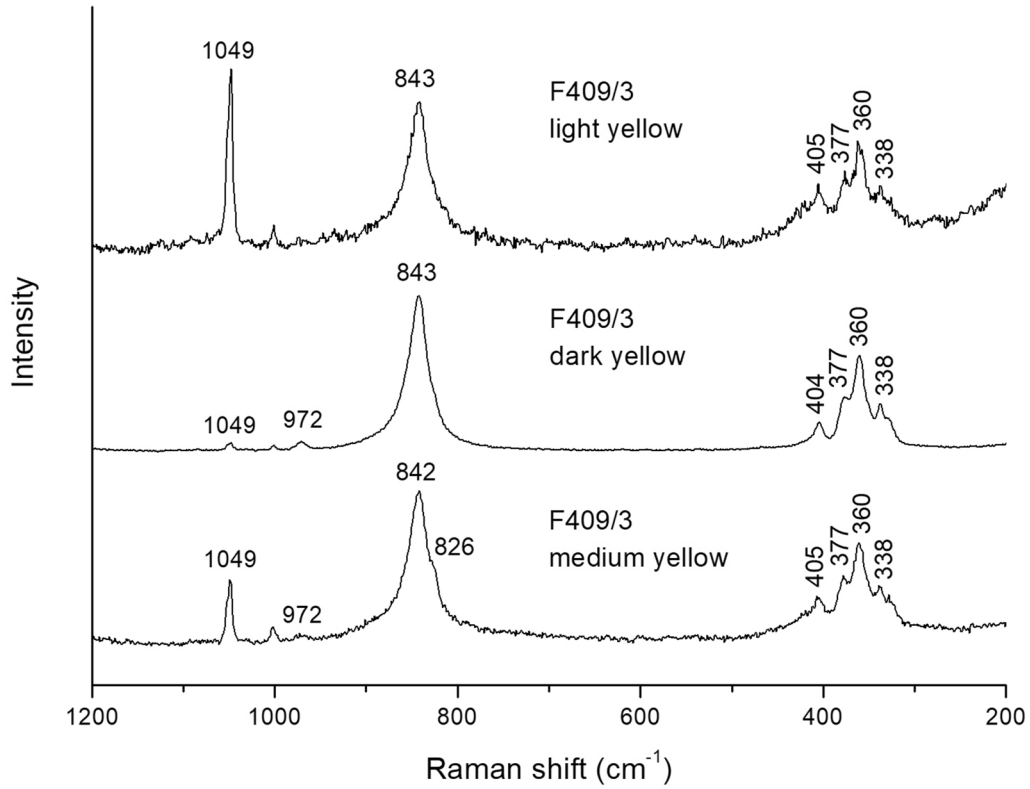

Fig. 7 Raman spectra collected from the three paint layers of cross section F409/3

Sample F409/6 was also analyzed with micro-Raman spectroscopy. The spectrum is rather noisy and shows weak bands at ca. 841, 403, 376, 359, and 337 cm^{-1}. These features point to $PbCr_{1-x}S_xO_4$ with $0.25 < x < 0.5$, but there is some uncertainty concerning the peak maxima. For this sample the SEM–WDX results seem to be more informative.

From our results it appears that Van Gogh used at least two different types of chrome yellow in *Field with Irises near Arles*: almost pure lead chromate ($PbCrO_4$) and chrome yellow with approximately equal amounts of sulphate to chromate ($PbCr_{0.5}S_{0.5}O_4$). In addition, a third variety with a fraction of lead(II) sulphate between 24 and 42 mol% might be present. Monico et al. [6] distinguished three different varieties of chrome yellow in the paintings that Van Gogh made in Arles: monoclinic $PbCrO_4$, monoclinic $PbCr_{1-x}S_xO_4$ with $x < 0.5$ and monoclinic and possible orthorhombic $PbCr_{1-x}S_xO_4$ with $x \geq 0.5$.

On 11 April 1888, Van Gogh received three types of chrome yellow from the Paris supplier Tasset et L'Hôte: Chrome 1, Chrome 2 and Chrome 3, described as 'lemon', 'yellow' and 'orange' respectively.[5] It is likely that Van Gogh used these paints when creating *Field with Irises near Arles* in May 1888. The almost pure lead chromate probably corresponds to the yellow Chrome 2, while the sulphur-rich variety must match the lemon Chrome 1. Chrome 3, the orange variety, probably contained chrome orange [11, 31, 32]. Van Gogh also bought painting materials from an Arles supplier before he started to purchase his materials via his brother Theo in Paris in April 1888. In the case that the third intermediate variety identified in *Field with Irises near Arles* is not a mixture of chrome yellows 1 and 2, then it might, instead, be a separate tube paint that was obtained locally.

Conclusions

Using SEM–WDX analysis, different types of chrome yellow ($PbCr_{1-x}S_xO_4$) can be distinguished based on the quantification of the sulphur-content of the pigment. This identification can be performed on paint cross-sections, allowing for distinction between chrome yellows in different paint layers. Using this method, at least two different types of chrome yellow in *Field with Irises near Arles* were identified: almost pure lead chromate ($PbCrO_4$) and chrome yellow with approximately equal amounts of sulphate to chromate

[5] Letter 595 from Vincent van Gogh to Theo van Gogh, Arles, on or about Wednesday, 11 April 1888.

($PbCr_{0.5}S_{0.5}O_4$). In addition, a third variety with a fraction of lead(II) sulphate between 24 and 42 mol% might be present.

Comparison with Raman spectroscopy showed that SEM–WDX is rather more accurate, because it allows the lead(II) sulphate fraction to be determined within 1 mol% absolute, whereas with Raman spectroscopy only relatively broad ranges can be defined. The sensitivity of SEM–WDX seems to be comparable to Raman spectroscopy; a detection limit of around 5 wt% for lead chromate sulphate ($PbCr_{0.5}S_{0.5}O_4$) in lead white was determined for both techniques. According to Monico et al. [20] using Raman spectroscopy the detection of sulphur-rich $PbCr_{1-x}S_xO_4$ in mixtures with monoclinic $PbCrO_4$ is only possible if the former is present in sufficiently high concentrations. On the contrary, SEM–WDX is capable of detecting sulphur in such mixtures with low concentrations of lead chromate sulphate. In mixtures the result is an average of the sulphur-content and therefore, the technique can not differentiate between the varieties of chrome yellow present. Also other sulphur-containing pigments or fillers, such as barium sulphate, might contribute to the sulphur-signal detected with SEM–WDX which complicates the analysis. With the exception of lead(II) sulphate, the presence of these materials are not expected to hinder the identification of sulphur-rich $PbCr_{1-x}S_xO_4$ by Raman spectroscopy.

Paint cross-sections of the paintings examined in the current cataloguing project, as well as those available from previous studies, will be investigated with SEM–WDX by the authors. Van Gogh purchased his paints from several suppliers, each of which sold a number of hues of chrome yellow paint. It is expected to find differences in composition not only between the hues offered by each of them, but also between the paints sold by different suppliers. Correlation between the paint orders in Van Gogh's letters and the chrome yellows identified on his paintings will provide us with information about the specific pigment compositions of these paints. Moreover, the project will give us the unique opportunity to study the relation between the variety of chrome yellow used and its degradation in situ. This degradation includes not only darkening, but also softening and loss of coherence of the paint layer.

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Authors' contributions
RH and MG designed and run the SEM–WDX experiments, and IvdW performed the micro-Raman spectroscopy. All authors contributed in writing the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials
The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing interests
The authors declare that they have no competing interests.

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