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Louisiane Verger, Olivier Dargaud, Mathieu Chassé, Nicolas Trcera, Gwenaëlle Rouse, et al.. Synthesis, properties and uses of chromium-based pigments from the Manufacture de Sèvres. *Journal of Cultural Heritage*, 2018, 30, pp.26 - 33. 10.1016/j.culher.2017.09.012 . hal-01777923

**HAL Id: hal-01777923**

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Submitted on 25 Apr 2018

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Synthesis, Properties and Uses of Chromium-Based Pigments from the  
*Manufacture de Sèvres*

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## **Abstract**

Chromium (Cr) is at the origin of a wide variety of coloration (green, pink and brown) in porcelain glazes from the French *Manufacture de Sèvres*. This element was introduced for the first time at the factory in 1804, just a few years after its discovery by Louis-Nicolas Vauquelin. Pigments for glazes were developed at the laboratory of the factory, leading to a palette of 76 references. While the synthesis protocol and the nature of the precursors of these pigments are kept in laboratory notebooks, the products have never been characterized. In this work, the pigments composed of Cr were characterized by X-ray diffraction (XRD), UV-visible spectroscopy and X-ray absorption near edge structure spectroscopy (XANES). The analyses reveal the presence of common crystalline phases, and open new perspectives for the synthesis of pigments containing chromium at the *Manufacture de Sèvres*.

## **Keywords**

Pigments, chromium, color, Rietveld refinements, porcelain

## **1. Introduction**

Chromium was first discovered and isolated by Louis-Nicolas Vauquelin in 1797, from a crocoite ( $\text{PbCrO}_4$ ) sample from Siberia (N. L. Vauquelin 1797; Nicolas Louis Vauquelin 1797; Spiesser 1998). The name chromium, as proposed by Häuy (Vauquelin 1797) a prominent mineralogist who previously described the minerals emerald and beryl, originates from the word  $\chi\rho\omicron\mu\alpha$  (*chrôma*) meaning color in greek referring to its ability to impart various coloration to minerals, such as green for eskolaite  $\text{Cr}_2\text{O}_3$  and red for lead chromate

$\text{PbCrO}_4$ . Soon after this discovery, by analyzing ruby, spinel and emerald, Vauquelin has evidenced that a low content of chromium was responsible for the red and green colors of these three minerals (N. L. Vauquelin 1797; Vauquelin 1798a; Vauquelin 1798b; Spiesser & Fritsch 1998). Since then, numerous different colors have been attributed to this element due to its various oxidation states and chemical environments. Based on these discoveries, Vauquelin has already foreseen in his report to the « Journal de la Société des Pharmaciens de Paris » in 1797 (N. L. Vauquelin 1797), that the use of chromium oxides will provide “solid and nice colors to Painting and Enameller’s art”.

Chromium discovery paved the way for its rapid use in porcelain manufacturing. At that time in France, one of the most innovative institutions was the *Manufacture Impériale de Sèvres*; a manufacture producing since 1740 fine quality porcelain, mastering all stages of production and with a special attention to colors. In the early 19<sup>th</sup> century, under the vigorous impulsion of Alexandre Brongniart, chemist and director of the manufacture, chromium was used as pigment for deep green paints and background glazes. Brongniart might have known chromium possibilities thanks to his closeness with Haüy in Paris and his work at the *Mines de Paris* at the very same moment, as shown by its publication a few months earlier in the same journal as Vauquelin (Brongniart 1797). The development of chromium green colors appeared relatively simple since the color is obtained with the direct addition of the precipitated oxide in a lead flux to produce a glaze (Salvétat 1857; D’Albis 2003). The first trials of chromium based glazes at the manufacture date back to 1802 (Brongniart 1802; Préaud & Ostergard 1997). In 1806, the new green glazes obtained with chromium were used in production and subsequently replaced copper based green glazes (Brongniart 1854). During the first half of the 19<sup>th</sup> century, many chromates were also identified as potentially useful pigments: lead chromate (red), barium chromate (yellow-green) (Brongniart 1854), potassium

chromate (yellow) (Salvétat 1857), mercury chromate (red/violet and green) (Godon-Saint-Memin 1804) and iron chromate (Brongniart 1854).

In 1845, chromium green under-glaze is eventually introduced as a genuine marker of Sèvres porcelains with a mark stamped for each product (Préaud & Ostergard 1997) (Figure 1 (a)). The very same year, Brongniart called on a young scientist, Jacques-Joseph Ebelmen to be deputy director of the factory. When Brongniart died in 1847, Ebelmen succeeded Brongniart as the head of the factory. Besides his work to improve porcelain production, Ebelmen conducted research on the synthesis of minerals. Drawing its inspiration from solution chemistry, Ebelmen developed the crystalline growth method by the use of fluxes: precursors are mixed with a flux, such as boric acid or borax, and brought at high temperature in platinum foils. The flux plays the role of solvent at high temperature. Using this method, Ebelmen succeeded to synthesize some minerals for the first time, such as spinels (Ebelmen 1861). This crystalline growth method using fluxes initiated by Ebelmen is now commonly used to synthesize various compounds, including spinels (Halenius et al. 2010; Bosi et al. 2012; D'Ippolito et al. 2012; Andreozzi et al. 2001), garnets (Andrut & Wildner 2002; Lowell et al. 1971) or layered oxides (Hobbie & Hoppe 1988; Yubuta et al. 2009). After the sudden death of Ebelmen (1852), Alphonse Louis Salvétat, in charge of chemical works at the *Manufacture de Sèvres* until 1880, benefited from Ebelmen's experience and continued his work. The size of crystals obtained by Ebelmen or Salvétat was small, they were only observable under an optical microscope. However, since pigments are ground to be used in porcelain decoration, this new synthesis method was perfectly suited to obtain new pigments composed of chromium.

Brongniart and his successors are at the origin of series of new pigments composed of chromium oxides: research conducted at the laboratory leads to a palette of pigments which was finalized in the middle of the 20<sup>th</sup> century. Chromium is the most used coloring element

in the palette at Sèvres: among the 138 pigments regularly prepared, 76 are composed of chromium oxides (D'Albis 2003) and used in a wide range of temperature from 900°C to 1400°C. Pigments are regularly synthesized (Fig. 1 (b-c)) and mixed in different uncolored frits. The mixture is painted on porcelains and fired at high or low temperature. The uncolored frit vitrifies during firing and its role is to fix the color on the porcelain. Glazes are obtained, i.e. glassy decorative layers on the porcelain surface. Since 1882, laboratory notebooks have been kept to follow the production (Figure 1 (d)).

While the synthesis protocol of pigments is known (D'Albis 2003), the crystalline phases obtained after the thermal treatment have never been characterized and chromium speciation remained unknown. Such knowledge is essential to address (i) environmental issues associated with the toxicity of Cr<sup>6+</sup>, (ii) technical issues in order to better understand the history of synthesis of the pigments and (iii) scientific issues surrounding the origin of the colors of pigments. Furthermore, such analysis is mandatory to improve the coloring properties of the pigments from Sèvres and to update their synthesis. In this work, we characterize exhaustively the pigments composed of chromium from the *Manufacture de Sèvres*. By doing so, we have determined the crystalline nature of these pigments, allowing to propose a classification based on the Cr-bearing phases, and we have evidenced the chromium speciation, allowing to improve the synthesis processes and to understand the origin of the coloration.

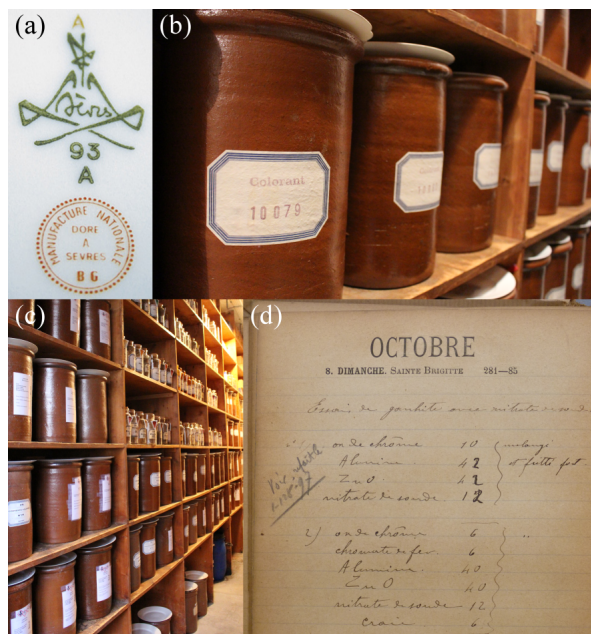


Figure 1: (a) Actual marker of Sèvres porcelains, the green color is obtain with chromium oxide  $\text{Cr}_2\text{O}_3$ ; (b-c) the storehouse of pigments in the laboratory of Sèvres manufacture; (d) snapshot of a laboratory notebook of 1893, describing the synthesis of a pigment.

## 2. Materials and methods

The pigments characterized in this work were taken from the collection of pigments of the Sèvres manufacture. The collection is composed of 138 references, indexed from 10001 to 10138, all available and regularly synthesized between a few grams to ten kilos. Only the 76 composed of chromium were characterized. Most of them are prepared by a classic ceramic route: metallic oxides are mixed, ground and then calcined at  $1280\text{ }^\circ\text{C}$  or  $1400\text{ }^\circ\text{C}$  in porcelain crucibles. The detailed historic synthesis of Sèvres pigments can be found in d'Albis (D'Albis 2003).

X-ray powder diffraction (XRD) data were collected using a PANalytical X'Pert PRO diffractometer with  $\text{Cu K}\alpha$  radiations ( $\lambda_{\text{Cu,K}\alpha 1} = 1.54056\text{ \AA}$ ,  $\lambda_{\text{Cu,K}\alpha 2} = 1.54439\text{ \AA}$ ) in the  $10^\circ$ - $130^\circ$   $2\theta$  range, with  $2\theta$  steps of  $0.008^\circ$  and a counting time of 25 s per step. Rietveld refinements (Rietveld 1969) were carried on some pigments out using the FullProf Suite program (Rodríguez-Carvajal 1993). This method is based on the least squares refinement of

structural model against the experimental XRD power pattern, and allows to obtain meaningful structural information (lattice parameters, atomic positions, bond lengths...) as well as phase quantification. The following parameters are refined: zero-shift, scale factor, background coefficients, lattice parameters, peak shape, atomic positions, atom occupancies, isotropic thermal parameter, microstructural parameters.

Diffuse reflectance spectra were recorded using a Perkin Elmer Lambda 1050 spectrometer equipped with an integrating sphere, between 4000-36,000  $\text{cm}^{-1}$ . The pigments were finely ground and the powdered samples were deposited on a support. A perfectly flat tablet of  $\text{BaSO}_4$  was used as a white reference material. Diffuse reflectance spectra of a powder are considered as representative of the absorption spectra but not completely equivalent due to particle size, refractive index and sample absorption coefficient (Lindberg and Snyder, *Am. Mineral.* 57(1972)485-493). A Kubelka-Munk conversion applied to a diffuse reflectance spectrum enables to obtain the absorption spectrum (Kubelka & Munk 1931).

X-ray absorption near edge structure (XANES) spectra at the Cr K-edge were collected on the LUCIA beamline at the SOLEIL synchrotron facility in Saint-Aubin (France). The synchrotron operated with a storage ring current of 450 mA and an energy of 2.75 GeV. The layout of the LUCIA beamline is described in Vantelon et al. (Vantelon et al. 2016). XANES spectra were collected using a Si(311) double crystal monochromator. The monochromator was calibrated against the maximum intensity of the first inflection of the first derivative of a metallic Cr standard (5989 eV). XANES measurements were performed in the energy range 5940-6200 eV. The energy steps were fixed to 2, 0.05, 0.2, 0.5 and 1 eV for energy ranges of [5940 - 5983] eV, [5983 - 5999] eV, [5999 to 6040] eV, [6040 - 6120] eV and [6120 - 6200] eV, respectively. Spectra were collected under vacuum at room temperature (around  $10^{-2}$  mbar) in X-ray fluorescence mode using a 4-elements Silicon Drift Diode detector. Samples were prepared in order to obtain pellets from powdered materials and were mounted on



carbon tapes. Two to four spectra were recorded for each sample with a counting time of about 1s per step. Multiple Cr K-edge XANES spectra recorded for each sample were merged to obtain average spectra before background subtraction and normalization using the ATHENA software (Ravel & Newville 2005).

### **3. Results and discussion**

#### **3.1. Classification of chromium-based pigments**

The color of each of the 76 pigments containing Cr of the Sèvres factory has been quantified using the chromatic parameters  $x$  and  $y$  in the system defined in 1976 by the International Commission on Illumination (abbreviated CIE). These parameters have been calculated from Kubelka-Munk converted diffuse reflectance spectra using the equation given by Wyszecki and Stiles (Wyszecki & Stiles 2008) (Figure 2). The pigments were also characterized by X-ray diffraction. Based on the nature of the crystalline phases determined by X-ray diffraction, five different groups of pigments were identified.

##### *3.1.1. The simplest chromium pigment: eskolaite ( $Cr_2O_3$ )*

Eskolaite ( $Cr_2O_3$ ) is the first chromium oxide used as a pigment at the *Manufacture de Sèvres* (Brongniart 1854; Ducrot 2008), giving a vibrant deep green color. Mixed with an uncolored frit, the pigment can be used directly to decorate porcelain artifacts. Thanks to its high stability in silicate melts, eskolaite was devised in decoration fired at high temperature, up to 1380°C. Eskolaite, mixed with calcium carbonate, quartz, kaolin or porcelain paste, is the precursor of four pigments (10035, 10065, 10085 and 10100). The resulting pigments after the thermal treatment consist of crystalline phases ( $Cr_2O_3$  and  $SiO_2$ ) mixed with a glass formed by the partial vitrification of quartz, kaolin or of porcelain paste. The purpose of this

process was certainly to lighten the green color of eskolaite. Four pigments using uranium or beryllium precursors are no longer used and, consequently, were not investigated.

### 3.1.2. Another green pigment: uvarovite ( $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ )

A series of pigment is historically obtained from potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), calcium carbonate ( $\text{CaCO}_3$ ) and quartz ( $\text{SiO}_2$ ). Uvarovite ( $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ ), also known as Victorian green (Colomban 2013), belongs to the garnet group and is the only chromium-bearing phase identified in these pigments by XRD after calcination. Trivalent chromium is localized in octahedral sites in this mineral (Sanchez Navas et al. 2004). Pigments composed of uvarovite are characterized by a green color, lighter than the one due to eskolaite (Figure 2).

The first synthesis of uvarovite at Sèvres is proven by a mention in the laboratory notebooks dating back to 1885. Furthermore, this kind of pigment is only used on one porcelain type (new hard-paste porcelain), the use of which started in 1882.

### 3.1.3. From green to pink along the solid solution $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$

Twelve pigments are obtained from eskolaite ( $\text{Cr}_2\text{O}_3$ ) and corundum ( $\text{Al}_2\text{O}_3$ ). The main phase identified by XRD in those pigments belongs to the solid solution  $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ , which color varies with chromium content from green to pink (Gaudry et al. 2005; Gaudry et al. 2003). Chromium(III) is in octahedral sites in the solid solution and it was previously shown by Gaudry et al. (Gaudry et al. 2005) that the modification of color can be ascribed to both the crystal field and the covalency of the Cr-O bonds, resulting from the broadening of the  $3d$  band by Cr-Cr coupling.

The first synthesis of corundum doped with chromium were conducted by Ebelmen in the kilns of the *Manufacture de Sèvres* and presented to “the Academy” in 1847 (Ebelmen 1861). Ebelmen obtained it by mixing alumina with borax, adding chromium oxide (1% of the

alumina mass), and calcining it on a platinum foil in a porcelain kiln. By this process, he obtained small transparent red crystals, embedded in an amorphous part. He isolated the crystals by the addition of hydrochloric acid at 70 °C or 80 °C. Ebelmen's works were continued by Salvétat to design new colored porcelain glazes. In the laboratory notebooks, numerous synthesis using alumina and potassium dichromate are reported. The pink color obtained is called "rose Salvétat" or "rose S.V.T".

#### 3.1.4. Tin-based pink pigments $\text{CaSnSiO}_5$ and $\text{SnO}_2$ doped with Cr

One pigment, called at Sèvres *Pink* or *Pinck*, is used to color porcelain glazes in a particular shade of pink (Faurel et al. 2003; Colomban et al. 2001). The main phase identified by XRD in this pigment (pigment 10081) is Cr-doped malayaite ( $\text{CaSnSiO}_5$ ). The name *Pink* was kept since the introduction of this pigment in Sèvres from a British sample. At the beginning of the 19<sup>th</sup> century, the British industry had developed a pink pigment to color under-glazes on earthenware. The synthesis being secret, Brongniart asked Malaguti, chemist at the *Manufacture de Sèvres* in 1838, to find the composition of this pigment. Malaguti succeeded to obtain the chemical composition and to identify the elements necessary to retrieve the pink color, as well as unneeded constituents which were added on purpose to mask the real pigment elements (Gay-Lussac & Arago 1836; Bouillon-Lagrange et al. 1836). He identified the key role of calcium, tin, silica and chromium. His researches also led him to synthesize a new lilac pigment, by simply calcining tin oxide and chromium oxide, leading to Cr-doped cassiterite ( $\text{SnO}_2$ ). Malayaite and cassiterite were detected by XRD in one and five pigments, respectively, giving pink to lilac colors (Figure 2).

Chromium speciation in the malayaite and cassiterite structures is less straightforward than in the corundum structure. Authors agree on the presence of  $\text{Cr}^{4+}$  in both structures, mainly substituting for  $\text{Sn}^{4+}$  in octahedral symmetry (Lopez-Navarrete et al. 2003; Cruciani et al.

2009; Doménech et al. 2006; Heyns & Harden 1999). In the case of malayaite, a very small amount of  $\text{Cr}^{4+}$  in tetrahedral symmetry in substitution for  $\text{Si}^{4+}$  was also detected by optical spectroscopy (Cruciani et al. 2009; Lopez-Navarrete et al. 2003). Furthermore, the presence of  $\text{Cr}^{3+}$  substituting for  $\text{Sn}^{4+}$  with the formation of oxygen vacancies to accommodate the charge was evidenced by optical spectroscopy and X-ray and neutron diffraction (Cruciani et al. 2009). The distribution of chromium between tetrahedral and octahedral sites and its valence variability are certainly the reasons why the color of pigment composed of Cr-doped malayaite is known to be hardly reproducible, and strongly dependent on synthesis conditions such as thermal treatment, used fluxes or precursors (Faurel et al. 2003; Harisanov et al. 2003; Cordoncillo et al. 1998).

### 3.1.5. A wide color palette obtained with spinels

Spinel was synthesized for the first time at the *Manufacture de Sèvres* by Ebelmen, around the middle of 19<sup>th</sup> century. In 1847, he reported the synthesis of Cr-doped red spinel ( $\text{Cr}^{3+}:\text{MgAl}_2\text{O}_4$ ), chromite ( $\text{FeCr}_2\text{O}_4$ ) and magnesiochromite ( $\text{MgCr}_2\text{O}_4$ ) in the wood-kiln for porcelain at Sèvres. Ebelmen used also kilns from a manufacturer of buttons, Jean-Félix Bapterosses, which can maintain a constant temperature. With those kilns he succeeded to obtain colorless gahnite ( $\text{ZnAl}_2\text{O}_4$ ) and Cr-doped gahnite. In the laboratory notebooks from 1882, syntheses of spinels are frequent, representing more than 50% of the laboratory's production between 1882 and 1904.

The addition of various transition metals such as chromium or cobalt in the spinel structure leads to a wide range of colors (Biagioni & Pasero 2014). Spinel is indeed identified by XRD in a majority of pigments (59.2 %). Transition elements combined with chromium at the Sèvres laboratory are cobalt, iron and manganese. When chromium is used in low concentration in gahnite ( $\text{ZnAl}_2\text{O}_4$ ) or spinel ( $\text{MgAl}_2\text{O}_4$ ), pink colors are obtained (Verger et

al. 2015; Bosi et al. 2011; Ikeda et al. 1997). The addition of cobalt enables to explore colors from green-blue to blue (D’Ippolito et al. 2012). The use of iron and manganese leads to pink-brown to black shades (Figure 2).

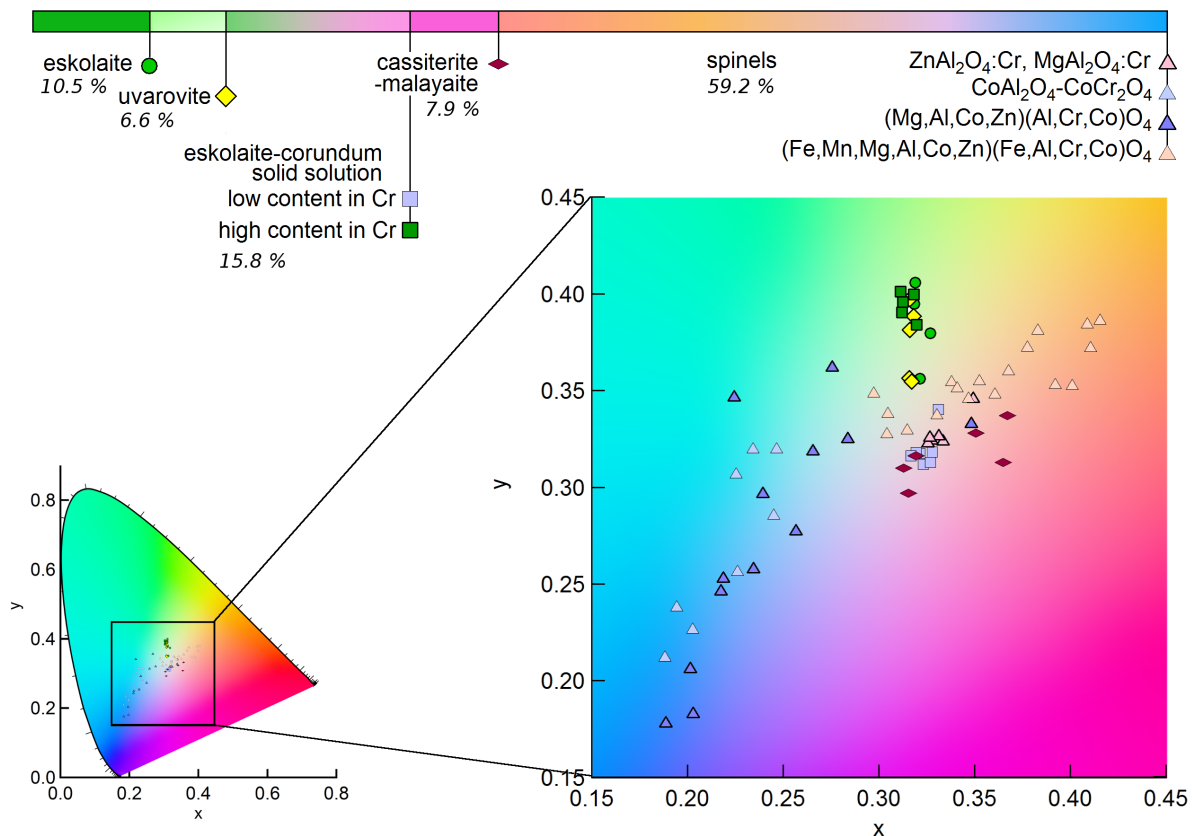


Figure 2: Chromaticity diagram ( $y$  as a function of  $x$ ) with the coordinates of the 76 pigments from the *Manufacture de Sèvres* containing Cr. The coordinates are calculated from the corresponding diffuse reflectance spectra. The percentage indicates the proportion of each type of pigments. Pigments obtained from uranium and beryllium precursors are not represented.

### **3.2. Principle of use of chromium oxides deduced from physical and chemical properties**

In this part, the most relevant observations and results obtained from the study of the series of pigments composed of chromium are reported, in order to distinguish common properties to the pigments and to open new perspectives for the synthesis of pigments.

#### *3.2.1. Chromium speciation*

Among the 76 pigments regularly synthesized at the laboratory, 18 were historically obtained from potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), a potential source for  $\text{Cr}^{6+}$ . The use of  $\text{Cr}^{6+}$  species is limited nowadays because of their high toxicity (Wetterhahn et al. 1989). Chromium (VI) is classified among carcinogenic agents, with the main effects on the respiratory system. Therefore, syntheses using  $\text{K}_2\text{Cr}_2\text{O}_7$  as a precursor were abandoned at Sèvres laboratory. However, these pigments were devised to give unique colors (light green, pink and lilac), and their interruption results in a considerable loss in porcelain decorations.

Pigments composed of uvarovite (3.1.2), corundum (3.1.3), malayaite or cassiterite (3.1.4) doped with chromium were obtained from  $\text{K}_2\text{Cr}_2\text{O}_7$ . One sample of each historical type was characterized by XANES spectroscopy at the Cr-K edge, respectively 10098 (uvarovite), 10059 (corundum), 10081 (malayaite) and 10095 (cassiterite). Pre-edge features are due to the s-d electronic transitions and is particularly sensitive to the presence of  $\text{Cr}^{6+}$  down to a few ppm (Peterson et al. 1997; Zachara et al. 2004; Villain et al. 2007). The absence of a symmetry center in the tetrahedral site of  $\text{Cr}^{6+}$  induces a strong absorption in the pre-edge region, as illustrated by the spectra of  $\text{K}_2\text{Cr}_2\text{O}_7$  in Figure 3 (a). Spectra of pigments 10098 and 10059 exhibit features typical of  $\text{Cr}^{3+}$  in uvarovite and corundum (Farges 2009; Gaudry et al.

2003). The pre-edge area of pigment 10081 is characterized by two features, at different energies from the one of  $\text{Cr}^{3+}$  in octahedral sites in  $\text{Cr}_2\text{O}_3$ . These two features are still not assigned, because of the complexity of Cr speciation in malayaite, and the poor solubility of Cr in malayaite which gives a bad signal to noise ratio (Lopez-Navarrete et al. 2003; Cruciani et al. 2009).

The pre-edge XANES spectra did not reveal any detectable  $\text{Cr}^{6+}$  in these pigments. Due to the sensitivity of the method (Peterson et al. 1997; Zachara et al. 2004; Villain et al. 2007), we can conclude that the  $\text{Cr}^{6+}$  precursor is reduced during the synthesis in  $\text{Cr}^{3+}$  and  $\text{Cr}^{4+}$ . The use of  $\text{K}_2\text{Cr}_2\text{O}_7$  as a starting material is thus not mandatory. The synthesis of pigments 10081 and 10098 have recently been modified at the laboratory of Sèvres by using  $\text{Cr}_2\text{O}_3$  as a precursor, based on the work of Andreola *et al.* (Andreola et al. 2008).

The spectrum of the historical pigment 10095 (cassiterite) presents a strong absorption band in the pre-edge region, characteristic of the presence of  $\text{Cr}^{6+}$ . Historically, to prepare the pigment after the calcination of the precursors, the product was grounded in water and the pigment was isolated by decantation. Former synthesis used  $\text{K}_2\text{Cr}_2\text{O}_7$  as a precursor and the water exhibited a yellow coloration, indicative of  $\text{Cr}^{6+}$  in solution (de Ruiter et al. 2008). For the purpose of the study, pigment 10095 was washed with water and removed by decantation. This process was repeated until the yellow coloration of the solution disappeared. Historical pigment 10095 before and after this process was characterized by UV-visible spectroscopy (Figure 3 (b)). The absorption band at  $27500\text{ cm}^{-1}$  (due to ligand-metal charge transfer between  $\text{O}^{2-}$  and  $\text{Cr}^{6+}$ ) disappears when the pigment is washed. Such observation indicates that  $\text{Cr}^{6+}$  species in pigment 10095 are highly soluble, and easily removed with water. The final concentration of  $\text{Cr}^{6+}$  in pigment 10095 was therefore uncertain in historical pigment preparation and was strongly dependent upon the washing step.

Our results indicate that no  $\text{Cr}^{6+}$  is needed for the final coloration, pleading for a substitution of chromates by less hazardous chromium species in the synthesis protocol.

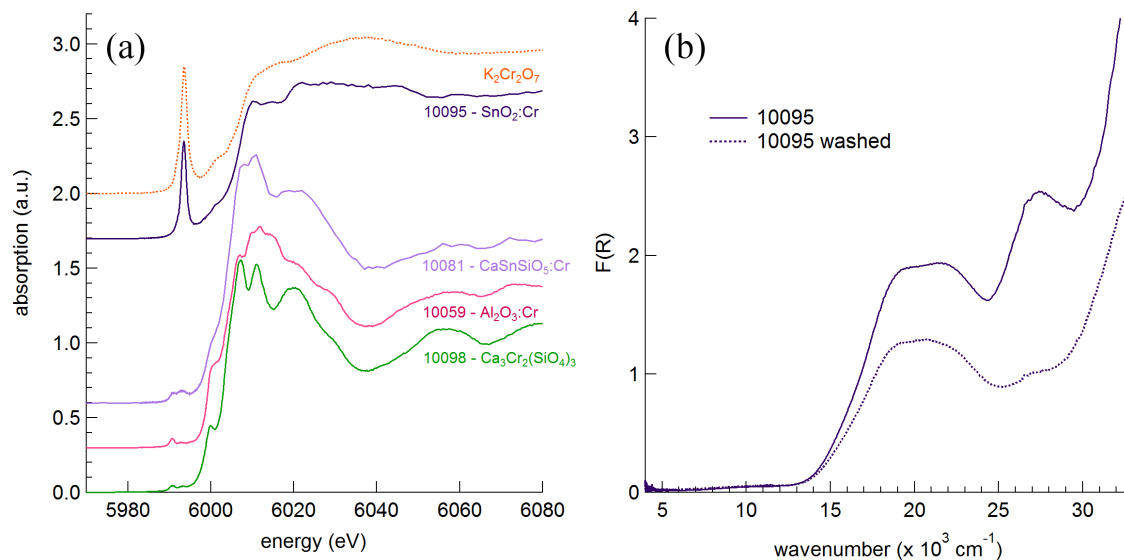


Figure 3: Analysis of pigments using potassium dichromate as a precursor. (a) XANES spectra at the Cr K-edge of pigments 10098, 10059, 10081, 10095 and a reference of potassium dichromate. (b) Diffuse reflectance spectra of pigment 10095, and pigment 10095 after washing.

### 3.2.2. Thermal treatment applied to the pigment

We have observed in several pigments from the spinel group that homogeneity in the pigment is not achieved after the thermal treatment, since a single spinel phase was not obtained. As an example, Figure 4 shows the XRD diagram of the pigment 10075, belonging to the spinel group. This pigment is obtained from  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$  and  $\text{Al}(\text{OH})_3$  after a heat treatment at  $1280^\circ\text{C}$ , the furnace being switched off as soon as the temperature is reached (no subsequent plateau). The heat treatment procedure was developed during the 19<sup>th</sup> century: pigments were calcined in wood-fired kilns, along with porcelain artifacts. The heat ramp was controlled to be slow enough to fire the porcelain and, once the desired firing temperature was reached, the kiln was turned off. It would have been particularly challenging at that time to



maintain a constant temperature with such kilns (Figure 4 (b)). After this thermal processing, several spinel phases are detected, each exhibiting distinct peak widths in the XRD patterns. However, when an annealing treatment at 1400 °C during 20 h is performed, the pattern of a single-phase with sharp diffraction peaks is obtained, corresponding to a spinel phase of homogeneous composition  $(\text{Al,Fe,Zn})(\text{Al,Cr,Fe})_2\text{O}_4$ . This shows that the firing treatment established in the 19<sup>th</sup> century does not allow a complete reaction during the synthesis of the pigment.

This protocol is still in use at the *Manufacture de Sèvres*. However, as we have shown for the pigment 10075, such heat treatment leads to multi-phase pigments. The proportion of the different phases is likely to vary according to the milling conditions, the quantity of pigment synthesized, and the kiln local properties and performances. The use of a plateau during the thermal treatment in modern furnaces will enable the formation of a single phase and improve the reproducibility between different productions of the same pigment.

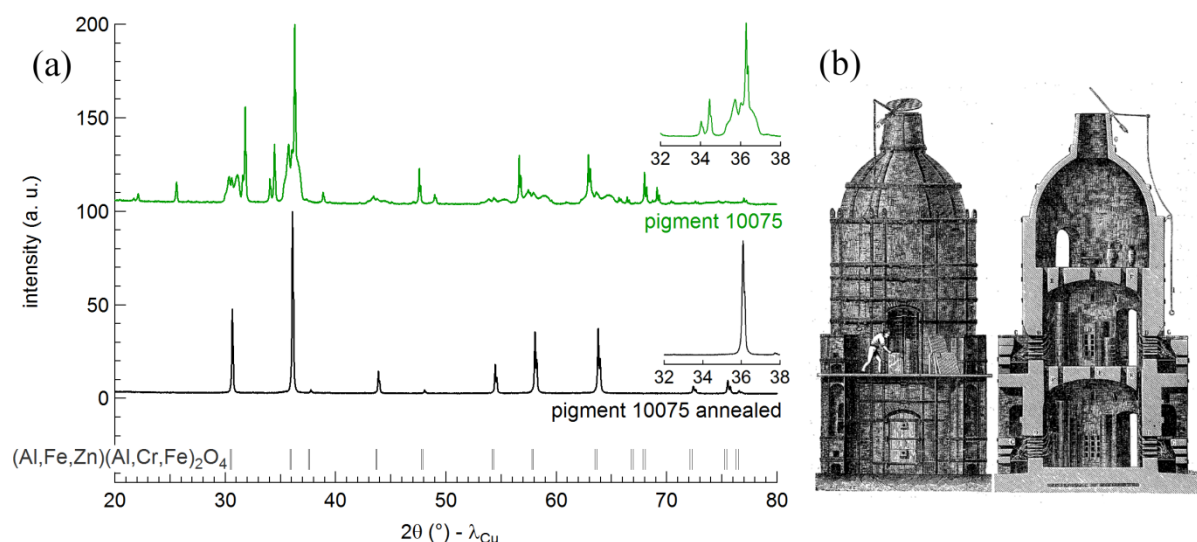


Figure 4: (a) XRD pattern of pigment 10075 before (green) and after (black) the annealing treatment at 1400 °C during 20h. Grey vertical tick marks indicate Bragg positions of spinel  $(\text{Al,Fe,Zn})(\text{Al,Cr,Fe})_2\text{O}_4$ . (b) Illustration of a wood-kiln in the Sèvres factory from *Les*

*merveilles de l'industrie ou description des principales industries modernes* (1876) by L.

Figuier (Figuier 1876).

### 3.2.3. Use of solid solutions

Various types of solid solutions were detected in pigments from Sèvres, such as  $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$  (corundum structure) or  $\text{MAl}_{2-x}\text{Cr}_x\text{O}_4$  ( $\text{M} = \text{Zn}, \text{Mg}, \text{Co}$ ) (spinel structure). However, the pigments do not cover the whole range of chromium concentrations, *i.e.*  $x = 0$  to 2. As a typical example, the end-members  $\text{CoCr}_2\text{O}_4$  and  $\text{CoAl}_2\text{O}_4$  were not detected by XRD for pigments mainly composed of the solid solution  $\text{CoAl}_{2-x}\text{Cr}_x\text{O}_4$ . Along this solid solution, spinel colors can vary from blue ( $x = 0$ ) to greenish blue ( $x = 2$ ) (Figure 5 (a)). Pigments containing  $\text{CoAl}_{2-x}\text{Cr}_x\text{O}_4$  spinels are prepared using  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CoCO}_3$  precursors. The Figure 5(a) illustrates the distribution of the nominal molar compositions of equivalent oxide precursors ( $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CoO}$ ) in the ternary diagram. We observe that all starting pigment compositions are offset with respect to the solid solution  $\text{CoAl}_{2-x}\text{Cr}_x\text{O}_4$ , represented by the horizontal line. As a consequence, the resulting pigments are composed of several phases. For instance, the Rietveld refinement indicates that pigment 10094 is composed in majority of spinel  $\text{CoAl}_{1.4}\text{Cr}_{0.6}\text{O}_4$  and in minority of spinel  $\text{Al}_{1.9}\text{Cr}_{0.1}\text{O}_3$  (Figure 5 (b)). Both lattice parameters and site occupancies can be fitted during the refinement and are in good agreement. Since lattice parameters and chromium occupancies are correlated by Vegard's law (Rossi & Lawrence 1970), the composition of the phase was determined using the lattice parameters.

Except pigment 10071, they are deficient in  $\text{CoO}$  content and have an  $\text{Al}_2\text{O}_3$  excess. Similar observations were obtained in  $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$  and  $\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$  solid solutions though nominal compositions were closer to the stoichiometric line.

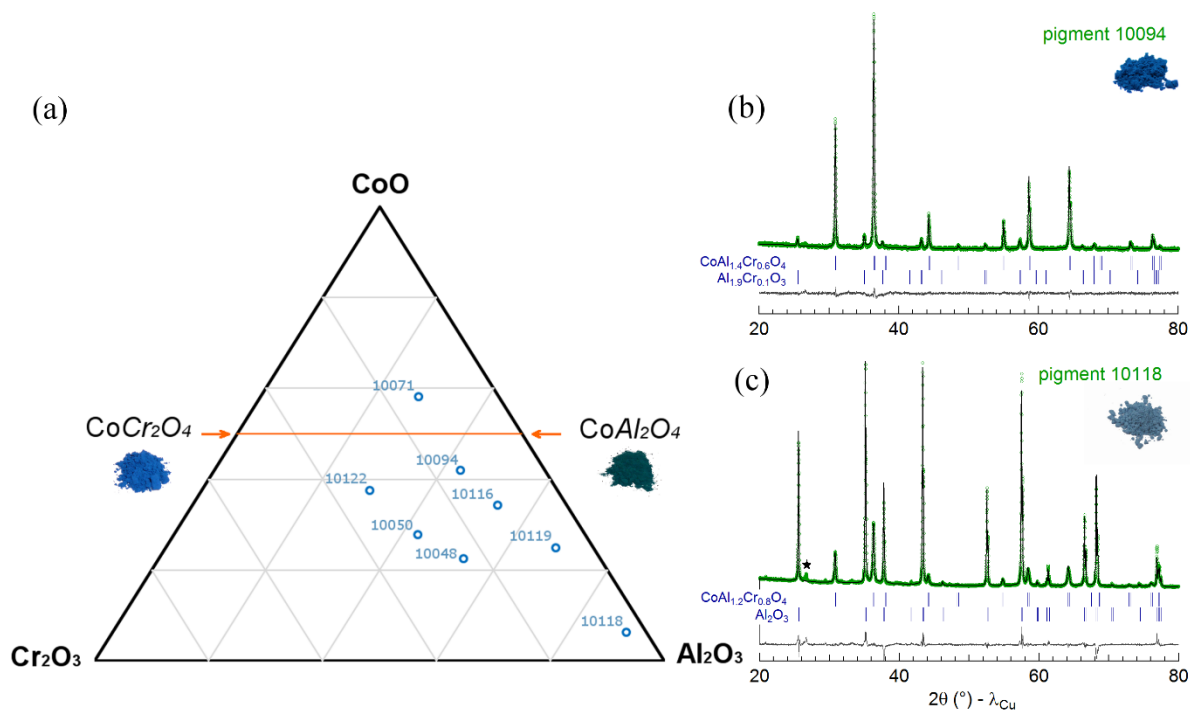


Figure 5: (a) Ternary diagram (mol%) CoO, Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>. The blue dots correspond to the precursors molar percentage used to synthesize the pigments. The orange line corresponds to composition along the solid solution CoAl<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub>. The two pictures illustrate the color of spinel phases CoCr<sub>2</sub>O<sub>4</sub> and CoAl<sub>2</sub>O<sub>4</sub>. (b-c) Rietveld refinements for pigments 10094 and 10118. The green dots are the observed intensities; the black line is the calculated intensity. Blue vertical tick marks indicate Bragg positions in space group Fd $\bar{3}$ m for CoAl<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub> and R $\bar{3}$ c for Al<sub>2-x</sub>Cr<sub>x</sub>O<sub>3</sub>. The peak indexed with a star corresponds to a quartz (SiO<sub>2</sub>) impurity.

### 3.2.4. Color attenuation

Pigments synthesized at the *Manufacture de Sèvres* are never composed of a single crystalline phase. Quartz (SiO<sub>2</sub>) was detected by XRD in almost every pigment (e.g., 10118 Figure 5 (c)), though it is not introduced as a precursor. This is probably due to a contamination from the porcelain crucible in which precursors are calcined. The impact of this contamination is limited because pigments are grounded with colorless frit composed of quartz in order to obtain the glaze.

As shown in the previous part (3.2.3), precursors are usually not introduced in stoichiometric proportion in the synthesis protocol of spinels  $MA_{2-x}Cr_xO_4$  (M=Zn, Mg, Co). For instance, the composition of pigment 10118 is the most distant from the stoichiometric line and is mainly composed of  $Al_2O_3$ , with a minority of  $CoAl_{1.2}Cr_{0.8}O_4$  (Figure 5(c)). Due to the presence of colorless  $Al_2O_3$ , the blue color is muted in pigment 10118 compared to pure  $CoAl_{1.2}Cr_{0.8}O_4$ . Similarly, malayaite and uvarovite are prepared with an  $Al_2O_3$  excess. The addition of an excess of colorless precursors such as  $Al_2O_3$  softens the saturation of the color and enables the modification of the shade of the expected pure phase.

The objective at Sèvres is not to obtain pigments composed of pure crystalline phases, but rather to get pigments with the most interesting and attractive colors, with different shades. Far from being an imperfection, the multiphasic aspect of Sèvres's pigments is a characteristic of the production of the *Manufacture de Sèvres* and, likely, it was purposely designed to obtain a vast and diverse palette of colors. This is also a signature of the process and the history of the production of pigments.

## Conclusion

The synthesis of chromium-based pigments at the laboratory of the *Manufacture de Sèvres* is linked to the discovery of this element at the end of the 18<sup>th</sup> century and the research conducted to synthesize minerals during the 19<sup>th</sup> century. This work puts in perspective the different type of pigments still synthesized nowadays with the history of the manufacture. Chromium is used as a precursor to obtain green and pink colors, and together with other transition metals, green-blue, brown and black colors. Despite the variety of colors in the pigments synthesized at the laboratory, six crystallized phases are evidenced, allowing the differentiation of five main groups: (1) eskolaite ( $Cr_2O_3$ ), (2) uvarovite ( $Ca_3Cr_2(SiO_4)_3$ ), (3) solid solution eskolaite-corundum ( $Al_{2-x}Cr_xO_3$ ), (4) Cr-doped cassiterite ( $SnO_2$ ) and malayaite

(CaSnSiO<sub>5</sub>), and (5) spinels. This work rationalizes the link between the crystallized phases identified in the pigment and their color on a wide set of pigments. The absence of Cr<sup>6+</sup> in the phases identified opens new perspectives for the synthesis of pigments avoiding environmentally hazardous Cr<sup>6+</sup> as a precursor. Eventually, this study highlights different approaches to set up a new palette of pigments composed of chromium, simplified and more complete: (i) synthesis of a unique crystalline phase, (ii) controlled variation of Cr occupancy over the whole solid solution in order to cover all possible shades, (iii) monitored dilution of every phase in colorless amorphous matrices (quartz, alumina for instance) in order to lighten the color.

### **Acknowledgements**

This work was supported by the Réseau Francilien sur les oxydes fonctionnels (DIM Oxymore) and the Région Ile-de-France. L. Verger acknowledges C. Bouttaz and D. Ratajczak for their help at the laboratory of Sèvres.

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# Synthesis, Properties and Uses of Chromium-Based Pigments from the *Manufacture de Sèvres*

## Supporting Information

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




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Table 1: Summary of the different type of pigments composed of chromium and synthesised at the *Manufacture de Sèvres*. Pigments 10028, 10029, 10030 and 10064 are not included (contain beryllium or uranium).

	Main phase composed of chromium	Chromium valency	Color	Number of pigments	Reference of pigments	Example
<b>Eskolaite</b>	$\text{Cr}_2\text{O}_3$	$\text{Cr}^{3+}$	Green	4	10035, 10065, 10085 <sup>‡</sup> , 10100	 10100
<b>Uvarovite</b>	$\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$	$\text{Cr}^{3+}$	Light green	5	10096, 10097, 10098, 10099, 10120	 10098
<b>Solid solution eskolaite-corundum</b>	$\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ ( $x > 1.9$ )	$\text{Cr}^{3+}$	Green	5	10005, 10027, 10046, 10123 <sup>¶</sup> , 10124 <sup>¶</sup>	 10046
	$\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ ( $x < 0.2$ )	$\text{Cr}^{3+}$	Pink	7	10003 <sup>§</sup> , 10018, 10019, 10020 10059, 10061, 10134	 10059
<b>Sn and Cr-based pigment</b>	$\text{CaSnSiO}_5 : \text{Cr}$	$\text{Cr}^{3+}, \text{Cr}^{4+}$	Pink	1	10081	 10081
	$\text{SnO}_2 : \text{Cr}$	$\text{Cr}^{3+}, \text{Cr}^{4+}$	Purple-pink	5	10079, 10086, 10087, 10088, 10095	 10095
	$\text{ZnAl}_2\text{O}_4 : \text{Cr}$	$\text{Cr}^{3+}$	Pink	4	10015, 10016, 10045, 10058	 10045
<b>Spinel</b>	$\text{MgAl}_2\text{O}_4 : \text{Cr}$	$\text{Cr}^{3+}$	Pink	2	10023, 10024	 10024
	$\text{CoAl}_{2-x}\text{Cr}_x\text{O}_4$	$\text{Cr}^{3+}$	Greenish blue to blue	8	10048, 10050, 10071, 10094, 10116, 10118, 10119, 10122	 10048
	$(\text{Mg}, \text{Al}, \text{Co}, \text{Zn})(\text{Al}, \text{Cr}, \text{Co})_2\text{O}_4$	$\text{Cr}^{3+}$	Pink, greenish blue, blue	13	10007 <sup>#</sup> , 10009, 10010, 10012 <sup>#</sup> , 10014, 10022, 10041, 10049, 10051, 10067, 10121, 10130, 10135	 10014
	$(\text{Mg}, \text{Al}, \text{Mn}, \text{Fe}, \text{Co}, \text{Zn})(\text{Al}, \text{Cr}, \text{Co}, \text{Fe})_2\text{O}_4$	$\text{Cr}^{3+}$	Dark green, brown, black	18	10004, 10008, 10025, 10026, 10039, 10040, 10043, 10044, 10052, 10054, 10074, 10075, 10077, 10078, 10084, 10091, 10101, 10132	 10075

□ calcium chromium oxide  $\text{CaCr}_2\text{O}_4$  is detected

¶ a spinel phase is detected as minority phase

§ a spinel phase and eskolaite are detected as minority phases

# willemite  $\text{Zn}_2\text{SiO}_4$  is detected as main phase

Table 2: Chromaticity parameters L\*, a\*, b\* of the pigments calculated from the diffuse reflectance spectra.

	Main phase composed of chromium	Reference	L	a	b
Eskolaite	Cr <sub>2</sub> O <sub>3</sub>	10035	53.76	-18.45	17.51
		10065	65.05	-11.34	15.08
		10085	32.76	-3.58	5.02
		10100	54.49	-16.11	15.32
Uvarovite	Ca <sub>3</sub> Cr <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	10096	87.66	-10.18	9.76
		10097	74.10	-22.28	19.88
		10098	83.66	-19.04	17.18
		10099	90.04	-9.16	9.68
		10120	76.83	-19.32	18.41
Solid solution eskolaite-corundum	Al <sub>2-x</sub> Cr <sub>x</sub> O <sub>3</sub> (x>1.9)	10005	40.18	-15.78	12.60
		10027	52.19	-16.86	15.82
		10046	45.12	-15.79	12.83
		10123	38.98	-10.26	10.27
		10124	38.31	-13.12	10.51
	Al <sub>2-x</sub> Cr <sub>x</sub> O <sub>3</sub> (x<0.2)	10003	64.52	2.72	5.39
		10018	82.30	8.95	-2.48
		10019	80.40	12.07	-4.05
		10020	81.20	7.84	-2.56
		10059	72.83	12.26	-2.86
10061	74.87	10.65	-1.11		
10134	33.54	3.75	-1.82		
Sn and Cr-based pigments	CaSnSiO <sub>5</sub> :Cr	10081	64.29	24.49	2.59
	SnO <sub>2</sub> :Cr	10079	61.42	13.41	4.64
		10086	73.72	14.63	-9.66
		10087	84.98	8.94	-6.58
		10088	64.92	7.13	-2.65
		10095	54.37	14.19	8.40
Spinel	ZnAl <sub>2-x</sub> Cr <sub>x</sub> O <sub>4</sub> (x<0.41)	10015	82.04	11.55	1.55
		10016	85.89	9.04	0.75
		10045	77.02	8.34	10.79
		10058	86.44	8.04	1.11
	MgAl <sub>2-x</sub> Cr <sub>x</sub> O <sub>4</sub> (x<0.44)	10023	83.33	8.72	-0.07
		10024	79.16	9.13	1.99
	CoAl <sub>2-x</sub> Cr <sub>x</sub> O <sub>4</sub>	10048	48.58	-23.05	-9.63
		10050	45.24	-17.73	-8.09
		10071	34.95	-5.31	-20.14
		10094	38.21	-5.23	-35.07
		10116	47.12	-13.35	-32.61
		10118	70.71	-12.40	-22.13
		10119	51.42	-5.66	-37.58
	10122	36.48	-18.50	-10.82	
	(Mg,Al,Co,Zn)(Al,Cr,Co) <sub>2</sub> O <sub>4</sub>	10007	36.82	-9.68	-5.71
		10009	54.94	2.90	-46.78
		10010	72.89	-3.32	-23.96
		10012	46.95	14.35	-49.48
		10014	63.69	-4.84	-30.11
		10022	43.76	9.53	-49.87
		10041	60.10	-17.42	-16.87
		10049	48.58	-23.05	-9.63
		10051	49.84	-8.71	-27.62
		10067	49.87	-20.19	3.09
		10121	45.35	-31.69	-4.65
		10130	75.94	12.98	6.59
		10135	52.71	-7.15	-30.84
	(Mg,Al,Mn,Fe,Co,Zn)(Al,Cr,Co,Fe) <sub>2</sub> O <sub>4</sub>	10004	29.24	-6.87	1.73
10008		24.91	-3.05	0.68	
10025		49.78	10.92	23.68	
10026		43.83	10.94	22.82	
10039		60.67	6.06	8.61	
10040		43.03	5.63	15.11	
10043		27.79	1.93	2.43	
10052		30.25	0.36	0.18	
10054		76.43	7.65	27.25	
10074		38.59	14.63	12.84	
10075		51.22	14.87	21.65	
10078		42.59	3.82	8.90	
10084		46.97	14.53	13.82	
10091		56.43	-2.28	-1.43	
10101	27.90	0.25	5.48		
10044	48.33	2.00	7.64		
10077	33.53	6.26	7.11		
10132	34.77	5.37	10.00		

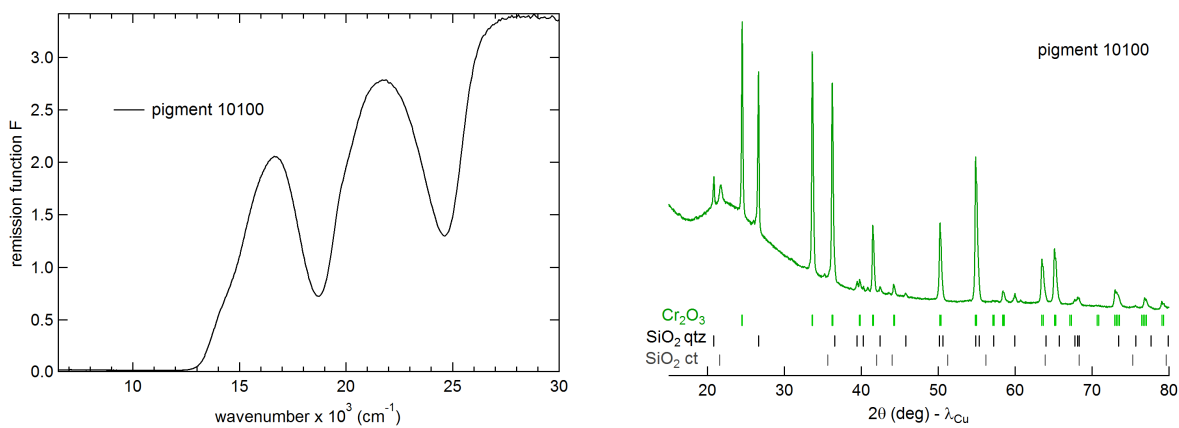


Figure 1: (left) Remission function  $F$  calculated from the diffuse reflectance spectra of pigment 10100 and (right) XRD diagram of pigment 10100 with the main phases identified:  $\text{Cr}_2\text{O}_3$ ,  $\text{SiO}_2$  quartz and  $\text{SiO}_2$  cristobalite.

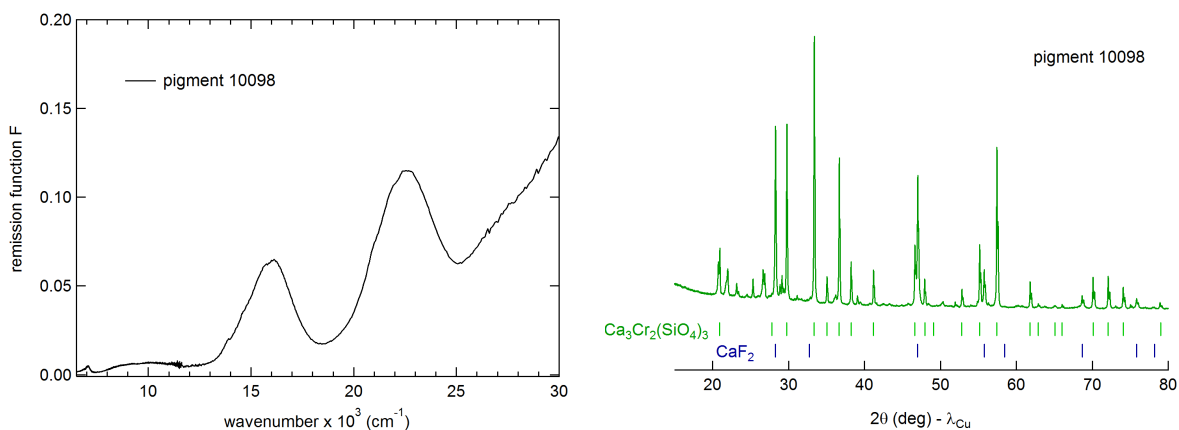


Figure 2: (left) Remission function  $F$  calculated from the diffuse reflectance spectra of pigment 10098 and (right) XRD diagram of pigment 10098 with the main phases identified:  $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$  and  $\text{CaF}_2$ .

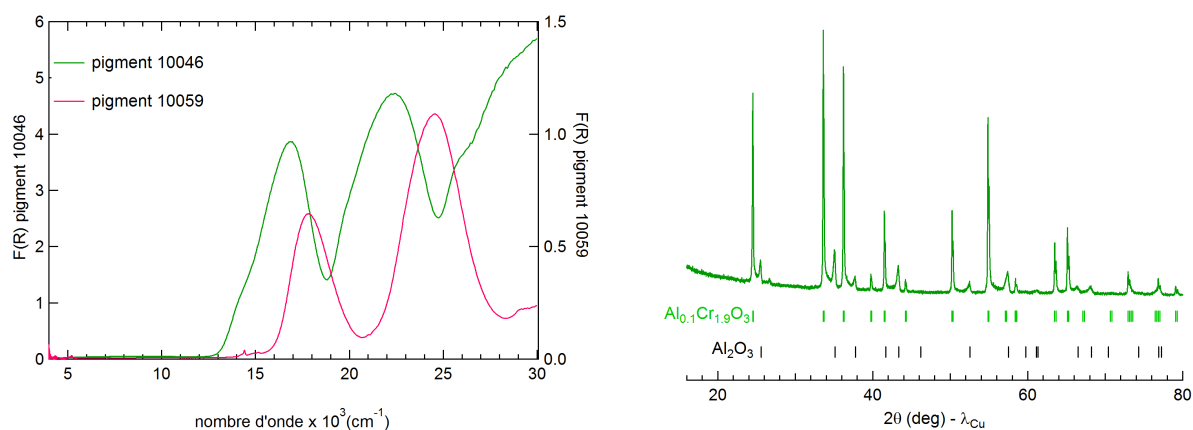


Figure 3: (left) Remission function  $F$  calculated from the diffuse reflectance spectrum of pigment 10046 and pigment 10059 and (right) XRD diagram of pigment 10046 with the main phases identified:  $\text{Al}_{0.1}\text{Cr}_{1.9}\text{O}_3$  and  $\text{Al}_2\text{O}_3$ .

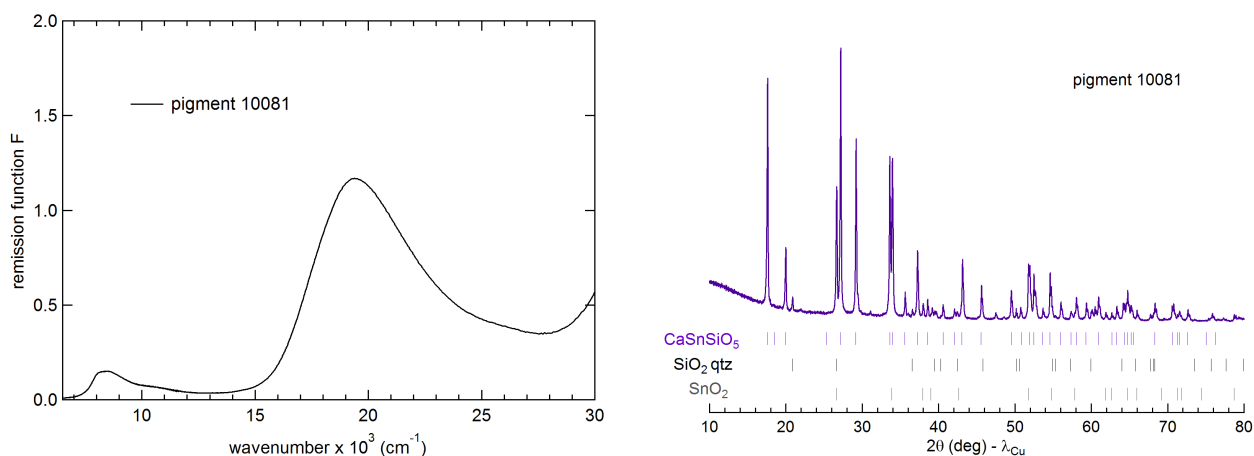


Figure 4: (left) Remission function F calculated from the diffuse reflectance spectra of pigment 10081 and (right) XRD diagram of pigment 10081 with the main phases identified: CaSnSiO<sub>5</sub>, SiO<sub>2</sub> quartz and SnO<sub>2</sub>.

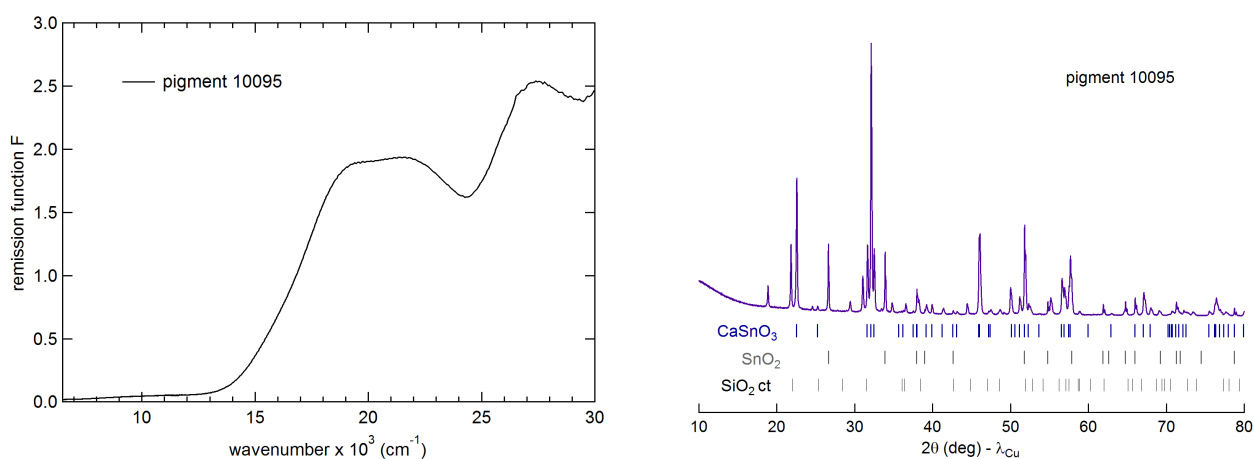


Figure 5: (left) Remission function F calculated from the diffuse reflectance spectra of pigment 10095 and (right) XRD diagram of pigment 10095 with the main phases identified: CaSnO<sub>3</sub>, SnO<sub>2</sub> and SiO<sub>2</sub> cristobalite.

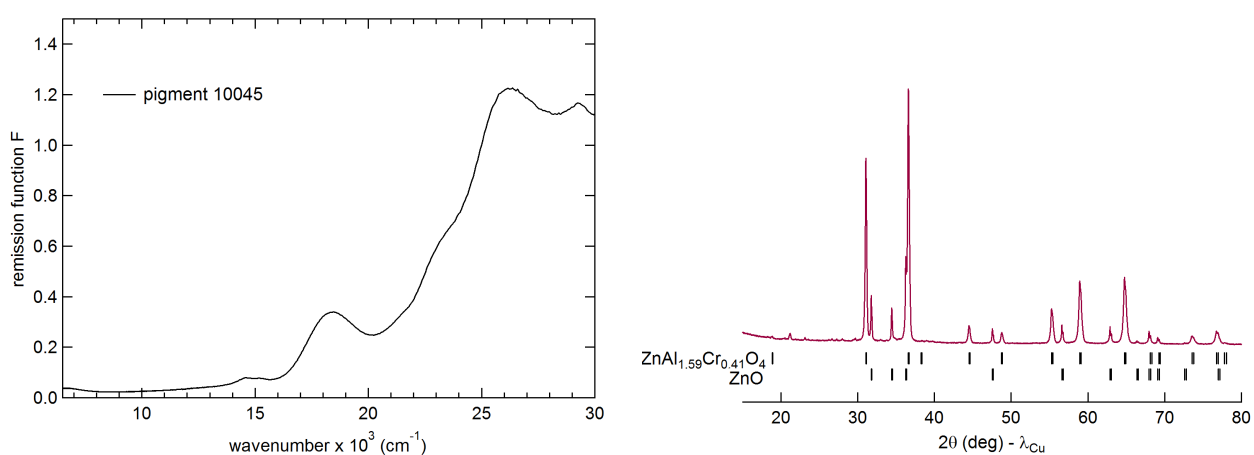


Figure 6: (left) Remission function F calculated from the diffuse reflectance spectra of pigment 10045. The high absorption in the near-UV region is due to the presence of ZnO, a semi conductor compound with a gap energy located at 26600 cm<sup>-1</sup>. (right) XRD diagram of pigment 10045 with the main phases identified: ZnAl<sub>1.59</sub>Cr<sub>0.41</sub>O<sub>4</sub> and ZnO.



Table 3: Rietveld refinement on pigment 10094: crystallographic data and atomic positions of the two phases  $\text{CoAl}_{1.4}\text{Cr}_{0.6}\text{O}_4$  and  $\text{Al}_{1.9}\text{Cr}_{0.1}\text{O}_3$ . Biso, atomic positions and occupancy are not fitted for the phase  $\text{Al}_{1.9}\text{Cr}_{0.1}\text{O}_3$  because of the low intensity of the characteristic peaks of the phase.

Pigment 10094  $\chi^2 = 2.434$

CoAl <sub>1.4</sub> Cr <sub>0.6</sub> O <sub>4</sub> $Fd\bar{3}m$ $R_{Bragg} = 11.2\%$ $a = 8.17661(5)\text{\AA}$ $V = 546.664(6)\text{\AA}^3$						
Atom	Wyckoff position	Occupancy	x	y	z	Biso ( $\text{\AA}^2$ )
Co	8a	1	0.125	0.125	0.125	1.01
Al	16d	0.7	0.5	0.5	0.5	0.49
Cr	16d	0.3	0.5	0.5	0.5	0.49
O	32e	1	0.26402(12)	0.26402(12)	0.26402(12)	0.86

Al <sub>1.9</sub> Cr <sub>0.1</sub> O <sub>3</sub> $R\bar{3}c$ $R_{Bragg} = 41.2\%$ $a = 4.77631(16)\text{\AA}$ $c = 13.0377(7)\text{\AA}$ $V = 257.583(18)\text{\AA}^3$						
Atom	Wyckoff position	Occupancy	x	y	z	Biso ( $\text{\AA}^2$ )
Al	12c	0.95	0.5	0.5	0.35217	1
Cr	12c	0.05	0.5	0.5	0.35217	1
O	18e	1	0.69365	0	0.25	1

Table 4: Rietveld refinement on pigment 10118: crystallographic data and atomic positions of the two phases  $\text{CoAl}_{1.2}\text{Cr}_{0.8}\text{O}_4$  and  $\text{Al}_2\text{O}_3$ .

Pigment 10118  $\chi^2 = 7.190$

CoAl <sub>1.2</sub> Cr <sub>0.8</sub> O <sub>4</sub> $Fd\bar{3}m$ $R_{Bragg} = 8.88\%$ $a = 8.20253(10)\text{\AA}$ $V = 551.878(12)\text{\AA}^3$						
Atom	Wyckoff position	Occupancy	x	y	z	Biso ( $\text{\AA}^2$ )
Co	$8a$	1	0.125	0.125	0.125	1.05
Al	$16d$	0.6	0.5	0.5	0.5	1.41
Cr	$16d$	0.4	0.5	0.5	0.5	1.41
O	$32e$	1	0.2622(5)	0.2622(5)	0.2622(5)	1.00

Al <sub>2</sub> O <sub>3</sub> $R\bar{3}c$ $R_{Bragg} = 9.06\%$ $a = 4.75930(2)\text{\AA}$ $c = 12.99156(6)\text{\AA}$ $V = 254.846(2)\text{\AA}^3$						
Atom	Wyckoff position	Occupancy	x	y	z	Biso ( $\text{\AA}^2$ )
Al	$12c$	1	0.5	0.5	0.35224(3)	0.56
O	$18e$	1	0.69136(15)	0	0.25	0.35