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# Non-invasive spectroscopic analyses of M. E. Chevreul's colour plates: shedding new light on 19<sup>th</sup> century colour theory representation

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## Abstract

During the early 19<sup>th</sup> century, colour's theories flourished. In this context, Eugène Chevreul (1786-1889) developed a three-dimensional hemispherical colour space, reproduced and used for several decades by manufacturers, scientists, artists, architects, gardeners and designers, among others, to easily identify and classify colours. Despite the major influence and variety of chromatic spaces created by E. Chevreul, they have been the subject of a few scientific studies until now. This study will provide new information on the evolution of the printing technique, the materiality and the visual appearance of six different colour circles printed in 1847, 1855, 1861 and 1864. A dedicated analytical methodology was implemented combining visible and near-infrared reflectance imaging, X-ray Fluorescence, Raman, Short-Wave InfraRed fibre optic reflectance and mid-InfraRed Fourier Transform spectroscopies. This material identification revealed the coexistence of newly synthesized inorganic pigments, such as lead chromate, Prussian blue or Emerald/Scheele green, with established organic and inorganic pigments, such as cochineal lake, vermilion or minium. This study revealed a temporal evolution of the printing technique that leads to an improved colour representation.

## Keywords

Graphic arts ; colour classification system ; non-invasive multimodal study ; 19<sup>th</sup> century printing techniques

## 1. Introduction

The 19<sup>th</sup> century represents a turning point in the history of colour theory and Eugène Chevreul's chromatic circle is still nowadays the symbol of this chromatic turn [1,2]. While colour theories proliferated such as those of Johann Wolfgang von Goethe, George Field and Ogden Rood, E. Chevreul's theory of contrast, illustrated by remarkable colour plates [3–6], stood out and established itself as a lasting reference in the field of colour and perception theory. The three distinct roles of this hemispherical colour space, clearly described by E. Chevreul, is an extremely concrete and easy-to-use tool to: 1) universally define colours, 2) visualize the mixing of two different coloured materials and 3) visualize the effect of simultaneous contrast; this former point being the concrete application of his law of contrast. These circles are used among others by neo-impressionists, fauvists, cubists artists [7–9] and scientists to characterize the colour of their newly synthesized pigments. Over time, they also inspired new modern colour classification systems [10,11]. As a result, the question of the influence of these chromatic circles in these different fields remains central.

This colour classification system has been disseminated in a variety of material forms. E. Chevreul first designed his system into the form of a three-dimensional hemispherical plate printed in black and white in 1839 [12]. Then he presented at the French Science Academy in 1851, a circle made out of tinted wool produced by the Gobelins factory's dyers [13]. Finally, in 1855 [4], 1861 [5] and 1864 [6], E. Chevreul had several chromatic circles reproduced using the chromochalcography printing method, in order to disseminate this classification system to a wider audience and made it universal. Each edition comprises ten chromatic circles: the first one with the 72 bold colours, which was used as a basis for the nine others that present an increasing proportion of black. Although the printing technique used for these plates is no longer innovative for their time, as mentioned by E. Chevreul in his book of 1864 [6], their visual quality and accurate reproduction reveals the great skill of the engraver René Digeon and printers (R. Digeon himself in 1855, 1861 and Lamoureux in 1864). Moreover, the printing of these chromatic circles took place during a major turning point of the 19<sup>th</sup> century with the development of new synthetic inorganic and organic inks [14–19]. Thus, the influence of the choice of materials and the printing technique on the visual aspect of this colour representation system has yet to be studied. The 1<sup>st</sup> chromatic circle and the colour gamut of the book of 1864 kept by the National Natural History Museum has already been the subject of a purely colorimetric study by F. Viénot [20,21]. The aim of this research is to propose a larger material and colorimetric study of several bold chromatic circles from different printed editions. A dedicated non-invasive and portable multimodal methodology, inspired from recent analytical studies on graphic arts [14,22–24], was carried out to preserve the light-sensitive printed colour plates. It combines Reflectance Imaging Spectroscopy in the Visible and Near InfraRed domain (VNIR-RIS), single point elemental analysis by X-ray Fluorescence spectroscopy (XRF) and Raman spectroscopy to study the presence of characteristic colorants and pigments in the coloured inks [25–27]. Additionally, the reflectance data were also used to compare the colour representation of the circles from a colorimetric point of view [28]. Fibre Optic Reflectance Spectroscopy (FORS) in the Short-Wave Infrared (SWIR) and Fourier Transform mid-InfraRed spectroscopy (mid-FTIR) were performed to further characterize binders, paper support and ink fillers [24,29].

This study will provide new information on the evolution of the printing technique, the materiality and the visual appearance of these circles through different editions, as well as an overview of the conservation state of these graphic arts.

## 2. Material and methods

### 2.1. The colour plates

E. Chevreul's chromatic circles were published in several editions during the 19<sup>th</sup> century. This study focuses in particular on four different versions, one printed in 1855 and held in Paris at the Bibliothèque Nationale de France (BnF), another published in 1861 by the French Academy of Sciences and held by the Signac's Archives [30]. Finally, one version edited in 1864 and a preliminary printed version dated from 1847, both held at the Muséum national d'Histoire naturelle (MNHN).

#### 2.1.1. BNF colour plates

The book (36 (ver.) x 27 cm (hor.)) printed by R.-H. Digeon in 1855 [4] has been analysed *in situ* at the BnF, Paris (accession number V-4527). The 1<sup>st</sup> chromatic circle of bold colour represented in the Figure

1a was analysed solely. The book is composed of 10 colour plates representing the 1<sup>st</sup> colour circle with an increasing quantity of black from 0/10 until 9/10. The circles are preceded by a short introductory text on the circle construction and its three different uses.

### **2.1.2. MNHN colour plates**

An edition of the book printed in 1864 [6] was provided by the central library of the MNHN, Paris (referenced Fol Res 56). This book measures 36 (ver.) x 27 cm (hor.). It is composed of 26 written pages describing in a first part the wool chromatic circle construction, in a second part the chromochalcography construction and finally, the three distinct roles of the chromatic circles. The last part corresponds to the 27 colour plates including the ten colour circles, several colour scales and a representation of the light spectrum. Each of the printed plates bears the words of the engraver, Digeon sc. and the printer, Lamoureux Imp. Only the first chromatic circle entitled “1<sup>st</sup> chromatic circle of M. Chevreul containing the bold colours” (Figure 1b) is the subject of this study.

Several other chromatic circles part of the MNHN box referenced “Ms Ch 7 cercles chromatiques (1847-1864)”, have been studied. It concerns two undated leaflets (35 (ver.) x 27 (hor.) cm) representing the 1<sup>st</sup> chromatic circle entitled “Figure 5” (Figure 1c). One of the leaflets has less saturated colours and will be cited as “leaflet 5A” (Figure 1d), while the other is entitled “leaflet 5”. The caption, in particular the typography is identical to the circle Figure 5 in the 1864 book of the BnF [6]. An additional circle part of this corpus is a leaflet (26 (ver.) x 23.7 (hor.) cm) dated from January 1847, printed by G. Silbermann and entitled “Typographic printing essay of the 1<sup>st</sup> chromatic circle by M. Chevreul”. This title is hand-annotated by this sentence: “comprising the three primitive colours in sixty-nine of their binary mixtures” (Figure 1e).

### **2.1.3. Signac’s Archives**

The edition printed by the French Academy of Sciences in 1861 [5] and owned by the neo-impressionist painter Paul Signac is part of the Signac’s archives, Paris [30]. This atlas is solely composed of colour plates: a representation of the light spectrum, the 10 chromatic circles and some colour scales. The first chromatic circle (Figure 1f) is the subject of this study.

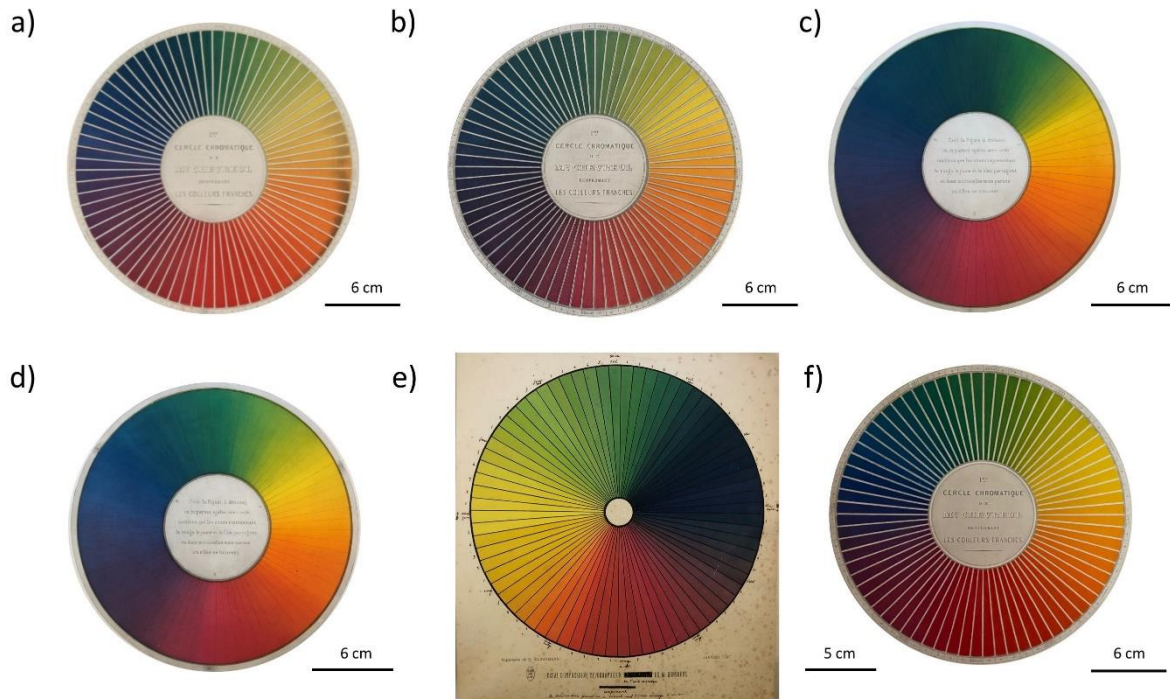


Figure 1. RGB images of the printed artworks analysed: a) 1<sup>st</sup> chromatic circle from 1855, 21 cm in diameter (ref. V-4527, BnF) [4], b) 1<sup>st</sup> chromatic circle from 1864, 21 cm in diameter (ref. Fol Res 56, MNHN) [6] and c) undated leaflet entitled Figure 5, 21 cm in diameter, d) undated leaflet 5A with less saturated hues, 21 cm in diameter, e) typographic essay from 1847, 25 cm in diameter (ref. Ms Ch 7, MNHN), f) 1<sup>st</sup> chromatic circle from 1861, 21 cm in diameter (Signac's Archives) [5].

## 2.2. Data acquisition and processing

### 2.2.1. Digital microscope observation

Microscope observations were performed using a digital microscope USB long working distance ©Edge Dino-Lite AM4815ZTL (Almere, Netherlands), with a resolution of 1.3 megapixels and available magnification from 10-140. The portable microscope is controlled by the software ©Dinocapture. Scales were added in the pictures thanks to the software ©ImageJ.

### 2.2.2. Diffuse reflectance imaging spectroscopy in the visible and near infrared domain (VNIR-RIS)

The reflectance spectra were acquired with a VNIR handheld push-broom Specim IQ camera commercialized by ©Specim (Oulu, Finland), covering a spectral range from 397 to 1003 nm with 204 bands wavelength channels (spectral resolution of 3 nm). The final hyperspectral cube has a spatial resolution of 512 x 512 pixels. The camera was mounted on a tripod at a distance of around 30 cm from the printed colour plates inclined at 45°. The colour plates were illuminated by two halogen lamps of 20 W set on a tripod on either side of the camera with a 45° incidence angle. Integration time was comprised between 50 and 80 ms. The data were normalized directly by the Specim camera using a white Spectralon® standard. Reflectance spectra were extracted from the cube using the software SpectronPro® (Resonon Inc, Bozeman MT, USA). The reflectance spectrum of each of the 72 hues of the colour circle corresponds to an average of 49 pixels. A spectral smoothing using a Savitzky-Golay filter (15 number of points, 2 polynomial degree) was performed. Hyperspectral datacubes were

directly converted into CIELAB coordinates using the plug-in CIE colour-space conversion from SpectronPro®[31] (S.I. A.). The original spectral range (397-1003 nm) was kept for calculation. Reflectance scale factor was set at 1. Illuminant D65 was chosen as well as a standard observer of 10°. An  $L^*$ ,  $a^*$  and  $b^*$  average and a standard deviation for the 72 hues of the circle were calculated on an average of 36 pixels (square of 6 x 6 pixels). The 72 hues of each circles were then plotted on a chromaticity diagram representing  $a^*$  as a function of  $b^*$ , with RGB values from the  $L^*$ ,  $a^*$  and  $b^*$  coordinates and the matlab function “labtorgb”.

### **2.2.3. X-Ray fluorescence spectroscopy (XRF)**

XRF was performed using a handmade portable single-point system. The collimated X-ray source is a Moxtek® MAGNUM (USA) Pd-anode tube, combined with a Silicon Drift Detector (SDD) with active area of 75 mm<sup>2</sup>, Amptek® (USA). The 1 mm X-ray beam strikes the surface of the sample with an incident angle of 45° while the detector remains perpendicular to the surface of the sample. The voltage used during the acquisition of the data was 30 kV and the current 100 µA for a total acquisition time of 150 ms per point. A teflon plate was placed under the historical paper sheet to limit inelastic scattering and prevent the analyses of the underlying circle or support. X-ray spectra were processed using the PyMca software [32].

### **2.2.4. Raman spectroscopy**

The Raman spectra were acquired with the spectrometer i-Raman ©BWTEK (New Jersey, USA) whose monochromatic laser is set at 785 nm. An average of 100 spectra per acquisition, covering a spectral range from 100 to 3010 cm<sup>-1</sup> (spectral resolution of 4.5 cm<sup>-1</sup>), was performed for a total acquisition time of 1000 ms. The spot of the laser is about 85 µm and its power was gradually increased from 5 to 25 %, to ensure the preservation of the area analysed while obtaining the best signal to noise ratio (SNR). The Raman spectra were processed using the software ©Spectragryph and a spectral smoothing using a Savitzky-Golay filter (13 number of points, 2 polynomial degree) was performed [33].

### **2.2.5. Fourier transform mid-infrared spectroscopy (mid-FTIR)**

Mid-infrared analyses were carried out in reflectance mode using a commercial Alpha II ®Bruker (Billerica, USA) instrument equipped with a Fourier transform spectrometer combined with a specular reflection module. Only leaflet colour circles were analysed using a homemade sample holder system, that allowed to place the sample parallel to the instrument, as well as the book dated from 1861 brought to the laboratory (Table 1). 256 scans were acquired over a range from 360 to 7500 cm<sup>-1</sup> (spectral resolution of 4 cm<sup>-1</sup>). FTIR spectra were studied using the software ©Spectragryph [33].

### **2.2.6. Fibre optic reflectance spectroscopy (FORS) in the short-wave infrared (SWIR)**

FORS-SWIR analyses were performed using a portable and contactless fibered near-infrared Fourier-transform spectrometer from ARCOptix® (Neuchatel, Switzerland), set on a homemade system mounted on a manual translation stage. The Rocket spectrometer is equipped with an interferometer permanently aligned with a dual retro-reflector and an uncooled InGaAs (Indium Gallium Arsenide) detector, whereas the light source is an ArcLight IR lamp. The spectra were collected through an optic fibre (Ocean Insight) with a 600 µm diameter at a working distance of 4 mm. An average of 100 spectra were acquired in the 1000–2500 nm (10,000–4000 cm<sup>-1</sup>) spectral range (spectral resolution of 2 cm<sup>-1</sup>). A plate of Spectralon® was positioned under the sheet to prevent the analysis of the underlying print colour. The spectra were processed using the software ©Spectragryph [33]. Due to time and access

constraints, the MNHN book dated from 1864, the typographic essay from 1847 and one leaflet were analysed using this approach (Table 1).

	VNIR-RIS	XRF	Mid-FTIR	FORS-SWIR	Raman
Typographic essay of 1847 (Figure 1e)	x	x	x	x	x
1 <sup>st</sup> colour circle of the book of 1855 (Figure 1a)	x	x			x
1 <sup>st</sup> colour circle of the book of 1861 (Figure 1f)	x	x	x		x
1 <sup>st</sup> colour circle of the book of 1864 (Figure 1b)	x	x		x	x
Undated leaflet 5 (Figure 1c)	x	x	x		x
Undated leaflet 5A (less saturated hues) (Figure 1d)	x	x	x	x	x

Table 1. Summary of the different analytical techniques used for each colour plates.

### 3. Results

#### 3.1. The printing technique

##### 3.1.1. Typographic essay of 1847

The 1847 coloured version of E. Chevreul's 1<sup>st</sup> chromatic circle could be a first attempt at printing, as suggested by the title (2.1.2), however technical information concerning the printing technique are absent. The Figure 2a, b and c illustrate the digital microscope observations of three different hues respectively the violet, green and orange-yellow. These observations show that each hue separated in quadrant, presents a different ink mixture. The 72 different inks were probably prepared by mixing several pigments beforehand and then applied separately on the paper. However, the printing technique could not be identified.

##### 3.1.2. The chromochalcography

The later circles dated from 1855, 1861 and 1864 were printed by the technique entitled chromochalcography. Digital microscopic observations highlight the use of at least 4 types of ink: yellow, orange, blue and red. The violet hue is obtained by the superimposition of the red ink on blue ink (Figure 2d). The green colour is the result of the superimposition of the blue ink on yellow ink (Figure 2e), whereas the orange ink is used for example to obtain the orange-yellow hue by its superimposition on the yellow ink (Figure 2f). The slight offset observed when two inks are printed successively, allows to define the different ink superimpositions and their chronological order of application. The random distribution of the ink dots and their relative uniformity of size around 0.1-0.2 mm, is reminiscent of the well-known aquatint. Indeed, this printing technique is based on the etching of steel plates with acid. The plates are previously coated with a resinous gum whose grains protect the steel from the acid attack. The time taken to soak in the acid and the space left between the resin grains produce delicate gradations from light to shadow and a visual aspect closed to the painting, which cannot be achieved with other techniques such as engraving with a burin [34,35]. The spaces between grains of resin are so tiny that they are not visible to the naked eye. The hue perceived

by the eye is the result of: 1) subtractive synthesis when the two inks perfectly overlap and 2) optical mixing when the two inks remain juxtaposed. More precise examples of these microscopic observations are given in the supplementary part (S.I. B).

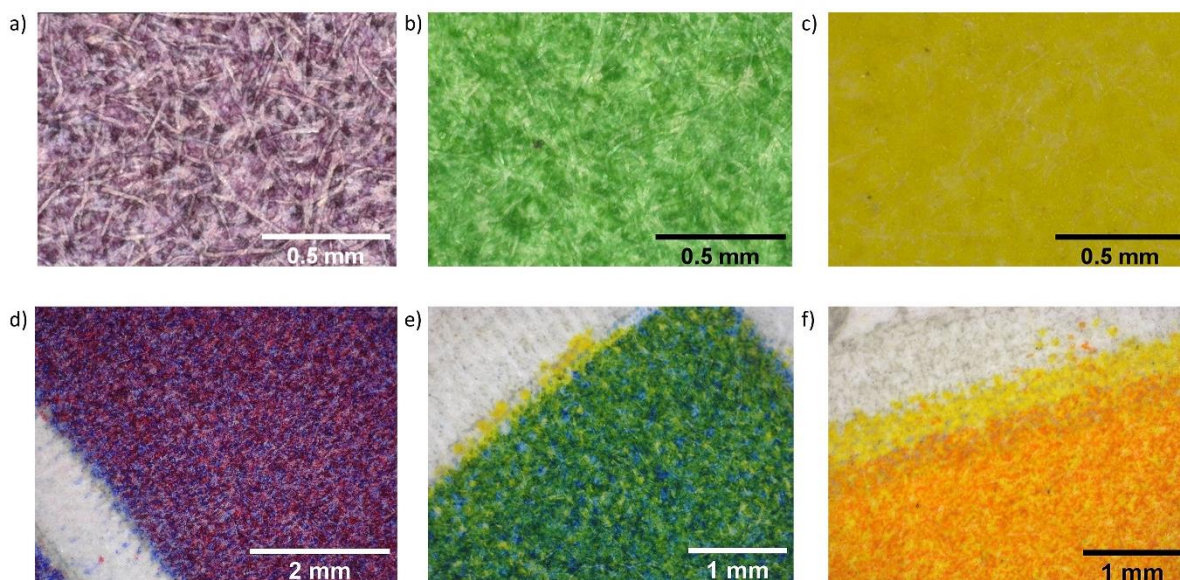


Figure 2. Microscope digital observations with ©Dinolite: a) violet, b) green, and c) orange-yellow hues of the typographic essay from 1847 (ref. Ms Ch7, MNHN) and d) violet, e) green, and f) orange-yellow hues of the 1<sup>st</sup> chromatic circle from 1855 (ref. V-4527, BnF) [4].

Crossing the digital microscopic observations with the article 2, preceding the chromatic circles from 1864 and entitled "Construction in chromochalcography", provides additional clues on the printing technique. It confirms that three inks are successively applied to obtain the 72 different hues, using three engraved steel plates: "His system is based entirely on the superimposition of colours, although the first circle is the result of only three superimposed colours [...] One worker prints yellow, a second applies blue on yellow, a third prints red on the application of blue on yellow, and a fourth worker, in a final print, superimposes black on the three colours" [36]. However, the orange ink is not mentioned in the book. This can suggest that R. Digeon probably had difficulty to obtain the orange hue by superimposing red on yellow ink. Additionally, this source confirms the microscopic observations highlighting a specific order in the printing of the different inks: yellow is printed first, then blue and finally red. From microscopic observation, orange is proposed to be printed between yellow and blue. However, no further information is given about the technique employed to engrave the steel plates. E. Chevreul only mentioned that R. Digeon is "not the inventor of this watercolour reproduction process" but "by dint of study and research, he has perfected the means and obtained results unknown until now." [36].

### 3.2. Material characterisation of chromatic circles

#### 3.2.1. Paper support

The mid-FTIR spectra of the paper supports for the leaflet 5, 5A, the 1847 and 1861 editions both show distinctive absorbance peaks characteristic of the cellulose, such as large absorbance bands at wavenumbers 3700-3100 cm<sup>-1</sup> (stretching vibration of OH groups in cellulose) and various bands over



the range 3000-2770  $\text{cm}^{-1}$  (CH stretching), 1470-1282  $\text{cm}^{-1}$  ( $\text{CH}_2$  bending vibrations) and 1200-895  $\text{cm}^{-1}$  (CO stretching, C–O–C and C–C–O bending vibrations) (Figure 3a). The presence of the band at 1507  $\text{cm}^{-1}$  (stretching of C=C aromatic) observed in Figure 3b, reveals that these papers are also composed of lignin and were made out from wood, a process that began in the mid-19<sup>th</sup> century with the development of industrial paper production [37]. The paper support of the 1847 circle has a much more degraded appearance, as evidenced by the multitude of brown spots (Figure 1e). Its mid-FTIR spectrum confirms these observations. The broad absorption band from 1750 to 1700  $\text{cm}^{-1}$  in Figure 3b indicates the presence of oxidized groups, i.e. carbonyl (C=O) or carboxyl (COOH) groups, while the absorption bands at 1058, 1031, 1012, 994  $\text{cm}^{-1}$  (C=O stretching, ring stretching and C-O-C asymmetric stretching vibrations respectively) illustrated in Figure 3c are characteristic of the presence of inter-intra ether bonds. These results confirm the photo-oxidation of cellulose and the advanced state of degradation of the paper [24,38]. Furthermore, additional absorption bands are observed for the papers of the leaflet 5, 5A and 1861 edition at wavenumber 876  $\text{cm}^{-1}$  (asymmetric  $\text{CO}_3^{2-}$  deformation) and 1793  $\text{cm}^{-1}$  ( $\text{CO}_3^{2-}$  symmetric stretching and in-plane bending) (Figure 3b, c) [29,39]. Together with the presence of calcium in the XRF spectra of these papers, these results suggest a calcite-based ( $\text{CaCO}_3$ ) preparation layer, not observed in the earlier version of 1847. The same calcite-based preparation layer is probably employed in the 1855 and 1864 edition, as suggested by the presence of Ca in the XRF spectra of these papers.

### **3.2.2. The chemical composition of coloured inks**

#### **3.2.2.1 Binder**

FTIR spectra acquired at the surface of all coloured inks analyzed show the presence of an absorption band centred at 1740  $\text{cm}^{-1}$  (C=O stretching of ester) together with the presence of an absorption at 2950  $\text{cm}^{-1}$  and 2860  $\text{cm}^{-1}$  (CH stretching of  $\text{CH}_3$  and  $\text{CH}_2$  respectively), visible in the Figure 3a-b. It confirms the use of an oil-based binder in the coloured areas. This result is in agreement with contemporaneous ink recipes, that mention the use of linseed oil as binder in various sources [18,40].

#### **3.2.2.2 Fillers**

An absorption band at 1793  $\text{cm}^{-1}$  and 876  $\text{cm}^{-1}$  is present in mid-FTIR spectra acquired in coloured inks, that corresponds to the presence of  $\text{CaCO}_3$  [29,39] (Table 2, and Figure 3b, c). The origin of the calcite is uncertain, as it may be present as an ink filler, or originate from the paper preparation, accessible between the ink coloured dots. The presence of a gypsum filler ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is also observed in the blue hue of leaflet 5A, shown in Figure 3c, with characteristic absorption bands at 3550  $\text{cm}^{-1}$  (OH stretching) and 1140  $\text{cm}^{-1}$  (asymmetric stretching vibration of  $\text{SO}_4^{2-}$ ) together with the doublet bands at 669  $\text{cm}^{-1}$  and 604  $\text{cm}^{-1}$  (asymmetric bending vibration of  $\text{SO}_4^{2-}$ ) [27].

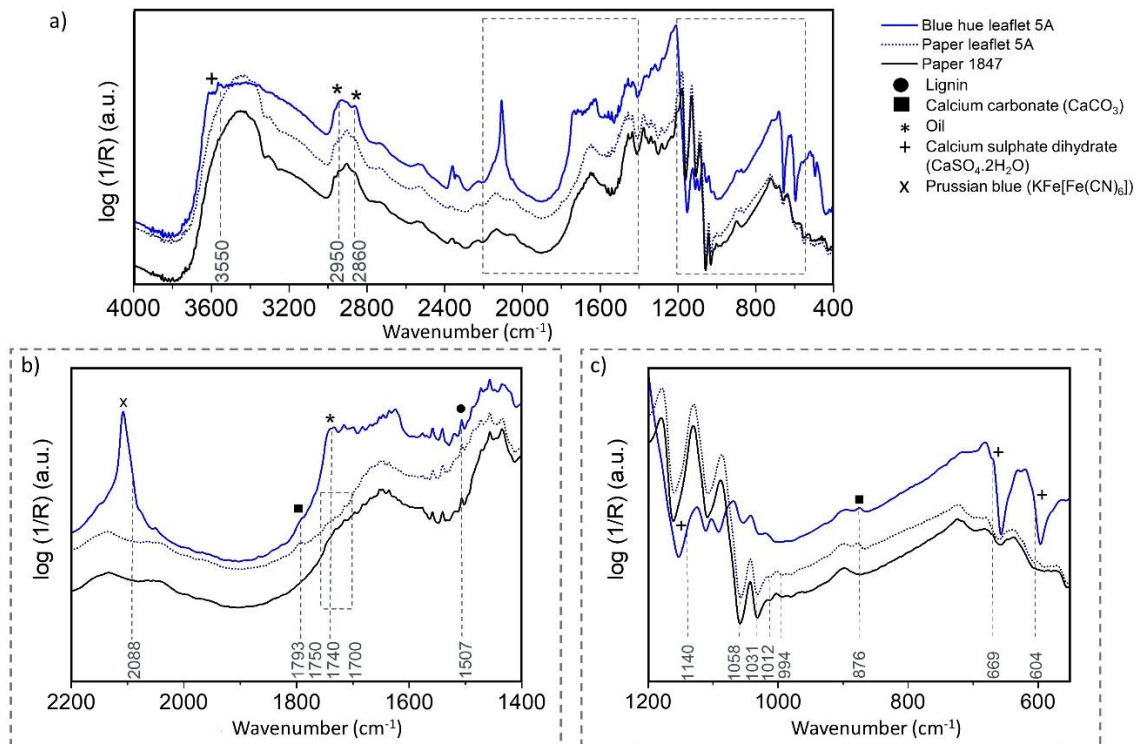


Figure 3. Mid-FTIR spectra collected on the leaflet 5A blue hue, paper of the leaflet 5A and paper of the 1847 circle, a) in the continuum domain 4000-400  $\text{cm}^{-1}$ , the dotted lines square represent the focused area in the b) 1400-2200  $\text{cm}^{-1}$  range and c) 650-1200  $\text{cm}^{-1}$  range.

### 3.2.2.3 Pigments

#### 3.2.2.3.1 Red inks

The reflectance spectra obtained by VNIR-RIS in all the red colours of circles entitled leaflet 5, 5A, 1855, 1861 and 1864 present two absorption bands at 522 nm and 562 nm characteristic of cochineal lake (Figure 4d). Aluminium or tin which could be assigned to the substrate are not detected by XRF. The presence of calcium in the XRF spectra can be attributed to the ink filler or to the substrate. However, the position of the characteristic absorption bands of the visible reflectance spectra do not match with the values suggested by Fonseca *et al.* in the case of a calcium-based substrate [25], such as the nature of the substrate stays unidentified. The two absorption bands of the 1847 red ink are less visible and the reflectance spectrum has a more pronounced sigmoidal shape (Figure 4a). In addition, the L-lines of Hg and K-lines of S in the XRF spectrum confirms the presence of the inorganic vermilion (HgS) pigment. The first red ink of 1847 is therefore a mixture of cochineal lake and vermilion.

#### 3.2.2.3.2 Blue inks

The blue ink of the circles dated from 1847, 1855, 1861, the leaflet 5 and 5A contains Prussian blue ( $\text{KFe}[\text{Fe}(\text{CN})_6]$ ,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ ) [41]. This inorganic pigment is characterized by mid-FTIR thanks to the cyano stretching vibration  $\nu(\text{CN})$  at 2088  $\text{cm}^{-1}$ , as shown in the mid-FTIR spectrum of the leaflet 5A blue hue in the Figure 3b. This result is also confirmed by the strong absorbance feature between 7500-11 000  $\text{cm}^{-1}$  and the narrow  $\nu(\text{CN})$  bands at 4220  $\text{cm}^{-1}$  and 4166  $\text{cm}^{-1}$  visible in FORS-SWIR [14,24,42]. An example of these characteristic bands in the blue hue of the 1847 edition is given in the Figure 4b and c. Additionally, the presence of K, and Fe in non-negligible quantities in the XRF spectra allows the identification of Prussian blue ( $\text{KFe}[\text{Fe}(\text{CN})_6]$ ) in editions from 1855 and 1861, in the absence of other characteristic chemical elements.

Analysis of the leaflet 5 and the circle from 1864 suggest the use of a mixture of Prussian blue, together with another pigment. While XRF spectra show high amounts of As and Cu (XRF), the mid-FTIR spectrum present the characteristic vibrational bands located at 817 and 770  $\text{cm}^{-1}$  ( $\nu(\text{As-O})$ ). Those results are leading to the identification of a copper arsenate green entering in the composition of the blue ink of those two circles, that could be Scheele or Emerald green ( $3 \text{Cu}(\text{AsO}_2)_2 \cdot \text{Cu}(\text{CH}_3\text{COO})_2$ ) [16,27].

#### 3.2.2.3.3 Yellow inks

The K-lines of Cr and L-lines of Pb in the XRF spectra of leaflet 5, leaflet 5A, and circles dated from 1847 to 1864, suggest the use of a yellow chromate pigment ( $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ ) as the main pigment of the yellow ink. Raman analysis allow a deeper characterisation of these pigments [27]. Thus, the chemical composition of lead chromate used for the two leaflets 5, 5A and the circle from 1855 and 1861 is  $\text{PbCr}_{0.4}\text{S}_{0.6}\text{O}_4$ , with the following characteristic peaks identified in Figure 4d:  $\delta(\text{CrO}_4^{2-})$  at 346 and 380  $\text{cm}^{-1}$ ,  $\delta(\text{SO}_4^{2-})$  at 438  $\text{cm}^{-1}$ , and  $\nu_s(\text{CrO}_4^{2-})$  at 843  $\text{cm}^{-1}$ . The yellow pigment of the circle of 1847 corresponds to the form  $\text{PbCr}_{0.5}\text{S}_{0.5}\text{O}_4$ , with the presence of  $\delta(\text{CrO}_4^{2-})$  at 360  $\text{cm}^{-1}$  and 378  $\text{cm}^{-1}$ , and  $\nu_s(\text{CrO}_4^{2-})$  at 843  $\text{cm}^{-1}$  (Figure 4d). The position and shape of the vibrational peaks of the circle dated from 1864 with  $\delta(\text{CrO}_4^{2-})$  at 339, 359.5, 378 and 402  $\text{cm}^{-1}$ , and  $\nu_s(\text{CrO}_4^{2-})$  at 841  $\text{cm}^{-1}$  (Figure 4d) confirm a lead chromate with a form  $\text{PbCr}_{0.7}\text{S}_{0.3}\text{O}_4$ . Additionally, a presence of Ba was also highlighted according to the XRF spectrum. Due to the absence of the characteristic Raman peaks for  $\text{BaCrO}_4$ , its presence is attributed to the possible use of baryte ( $\text{BaSO}_4$ ) as a filler agent.

#### 3.2.2.3.4 Orange inks

The Raman spectra acquired in orange hues from the leaflet 5, 5A, circle 1861 and orange-2 hue from the 1864 circle show two peaks at 123 and 550  $\text{cm}^{-1}$ , characteristic of the  $\nu(\text{Pb-O})$  vibrational band of minium ( $\text{Pb}_3\text{O}_4$ ) (Figure 4e) [43,44]. In addition, the sigmoidal shape of all the reflectance spectra and their inflection point at 565 nm corroborate this identification [26]. The orange hue of 1855 edition has not been analysed by Raman. However, the sigmoidal shape of the visible reflectance spectrum and its first derivative maximum at 566 nm, suggest that this orange ink is also composed of minium. The Raman spectrum of the 1847 orange hue shows only the peaks of the yellow chromate-based ink. In addition, the visible reflectance spectrum suggests a mixture of both a yellow pigment characterized by an absorption maximum at ca. 460 nm and another undetermined orange pigment, which leads to an inflection around 540 nm. The study of the adjacent colours does not allow the identification of this orange pigment. Indeed, the red-orange ink and red-orange-1 have different chemical compositions, respectively, vermilion identified by its three characteristic peaks at 254, 289  $\text{cm}^{-1}$  ( $\delta(\text{S-Hg-S})$ ), 346  $\text{cm}^{-1}$  ( $\nu(\text{HgS})$ ) [27] and minium, as shown in the Figure 4e.

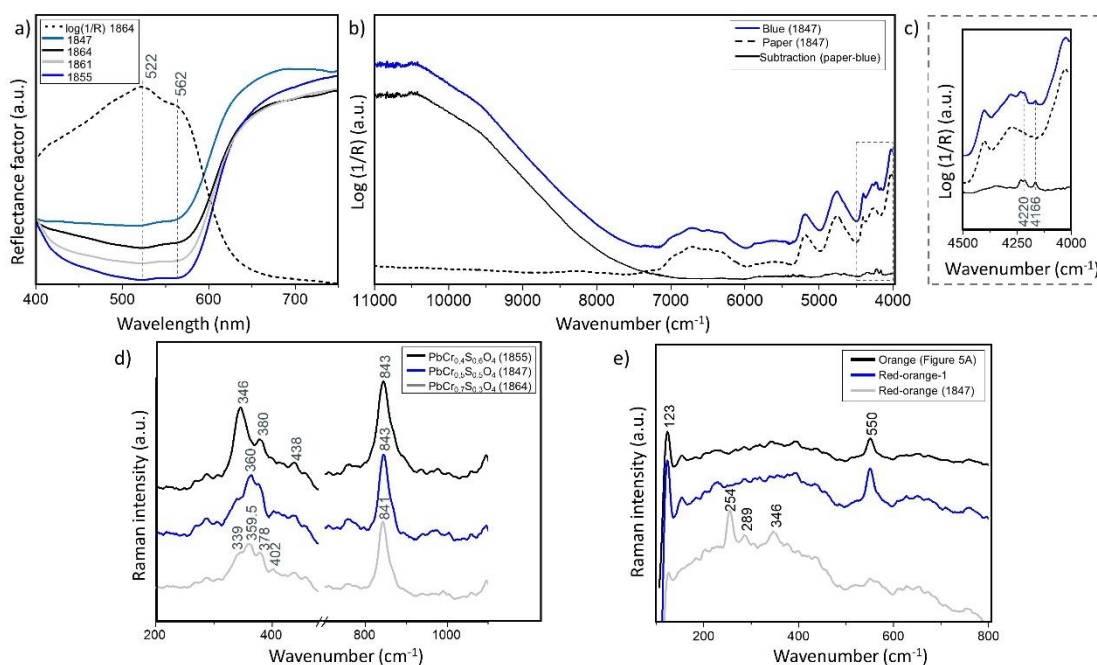


Figure 4. a) Visible reflectance spectra of the three red hues from 1847, 1855 and 1864, b) SWIR-FORS spectra comparison of the blue hue and the paper from 1847 (11 000-4000  $\text{cm}^{-1}$ ), dotted lines square represents the focused area in the 4000-4500  $\text{cm}^{-1}$  range presented in c), d) Raman spectra from the three yellow hues dated from 1847, 1855 and 1864, and e) Raman spectra of the orange (leaflet 5A) and red-orange hues (1847).

One can note that the part of the circle from 1855, made up of the superimposition of minium and chrome yellow, shows signs of degradation that corresponds to a darkening of the ink located on the right edges between orange-yellow-5 and red-orange-2 (Figure 1a). The visible reflectance spectra of these degraded hues, show a sharp decrease in reflectance from 570 nm to 1003 nm (S.I. C), different from the visible spectral changes observed during the photo-oxidation of lead chromate in linseed oil [45]. The degradation of the minium into galena ( $\text{PbS}$ ), known to cause paint layer blackening, could explain such visual change of the ink layer. This degradation product is formed when the minium is in the presence of a sulphur-based pigment, which could be chromium yellow  $\text{PbCr}_{0.4}\text{S}_{0.6}\text{O}_4$  [46,47]. Furthermore, microscopic observations of the orange hue presented in S.I. C show that the browning seems to affect the minium-based top layer. Nevertheless, a dedicated study with micro-samples would now be necessary to identify the degradation products responsible for this visual change.

Colour	1 <sup>st</sup> chromatic circle	XRF	VNIR-RIS (nm)	Mid-FTIR ( $\text{cm}^{-1}$ )	RAMAN ( $\text{cm}^{-1}$ )	SWIR ( $\text{cm}^{-1}$ )	L*a*b* coordinates (average)	Identification
Red	1847	Hg, S, Pb, (Fe, Ca)	522 <sup>a</sup> , 565 <sup>a</sup>	-	-	-	[56, 39, 18.5]	Vermilion, cochineal lake
	1855	Ca, S (Cr, Fe, Zn, Pb)	522 <sup>a</sup> , 562 <sup>a</sup>	-	-	-	[50, 50, 9.5]	Cochineal lake
	1861	Ca, S, Pb (Cr, Fe, Mn)	522 <sup>a</sup> , 562 <sup>a</sup>	-	-	-	[51.5, 44, 9]	Cochineal lake
	1864	Pb, Ca, S, (Fe)	522 <sup>a</sup> , 562 <sup>a</sup>	-	-	-	[47, 41, 10]	Cochineal lake
	Undated Leaflet 5	Fe, Ca, S	522 <sup>a</sup> , 562 <sup>a</sup>	876	-	-	[53.5, 40, 12.5]	Cochineal lake, calcium carbonate
	Undated Leaflet 5A	-	522 <sup>a</sup> , 562 <sup>a</sup>	876	-	-	[52.5, 40, 14]	Cochineal lake, calcium carbonate

Blue	1847	Fe, K, Pb, Ca, Cr, S	477 <sup>r</sup> , 600 <sup>a</sup>	2088	-	4220 7500-11000	[31, -5, -13]	Prussian blue
	1855	Fe, Ca, K, S, (Cr, Pb)	452 <sup>r</sup> , 422 <sup>i</sup> , 600 <sup>a</sup>	-	-	-	[40.5, -4, -27]	Prussian blue
	1861	Fe, Ca, S, (Pb)	472 <sup>r</sup> , 600 <sup>a</sup>	2088	-	-	[46.5, -13.5, -21.5]	Prussian blue
	1864	Cu, Fe, K, S, Ca, Pb, (Ba, Cr, As, Zn)	481 <sup>r</sup> , 600 <sup>a</sup>	-	-	4220 7500-11000	[38, -12, -15]	Prussian blue, Scheele or Emerald green, barium sulfate
	Undated Leaflet 5	As, Cu, Fe, Ca, S, (K, Ba)	477 <sup>r</sup> , 600 <sup>a</sup>	2088 770, 817	-	4220 7500-11000	[34, 9, -16]	Prussian blue, Scheele or Emerald green
	Undated Leaflet 5A	-	460 <sup>r</sup> , 600 <sup>a</sup>	2088 876 604, 669, 3550	-	-	[43, 8, -15]	Prussian blue, calcium carbonate, gypsum
Yellow	1847	Cr, Ca, Pb, S, (Fe)	sigm. 450 <sup>a</sup> , 507 <sup>d</sup> , 680 <sup>i</sup>	834, 860, 888, (v <sub>as</sub> CrO <sub>4</sub> <sup>2-</sup> ) 629, 599 (δ <sub>as</sub> SO <sub>4</sub> <sup>2-</sup> )	360, 378, 843	-	[74, -5, 52]	Chrome yellow (PbCr <sub>0.5</sub> S <sub>0.5</sub> O <sub>4</sub> )
	1855	Pb, Cr, Ca, S, (Fe)	sigm. 466 <sup>a</sup> , 507 <sup>d</sup>	-	346, 380, 438, 843	-	[76, 8, 50]	Chrome yellow (PbCr <sub>0.4</sub> S <sub>0.6</sub> O <sub>4</sub> )
	1861	Pb, Cr, Ca, S, (Fe)	sigm. 466 <sup>a</sup> , 507 <sup>d</sup>	593, 624 (δ <sub>as</sub> SO <sub>4</sub> <sup>2-</sup> ), 830, 870, 900 (v <sub>as</sub> CrO <sub>4</sub> <sup>2-</sup> )	346, 843	-	[78.5, 7, 55.5]	Chrome yellow (PbCr <sub>0.4</sub> S <sub>0.6</sub> O <sub>4</sub> )
	1864	Cr, Ba, Pb, Ca, S, (Fe)	sigm. 450 <sup>a</sup> , 517 <sup>d</sup>	-	339, 359.5, 378, 402, 841	-	[77, 7, 60]	Chrome yellow (PbCr <sub>0.7</sub> S <sub>0.3</sub> O <sub>4</sub> ), barium sulphate
	Undated Leaflet 5	Cr, Pb, Ca, S, (Fe)	sigm. 450 <sup>a</sup> , 507 <sup>d</sup>	593, 624, (δ <sub>as</sub> SO <sub>4</sub> <sup>2-</sup> ), 830, 870, 900 (v <sub>as</sub> CrO <sub>4</sub> <sup>2-</sup> )	346, 380, 438, 843	-	[73, 4, 59]	Chrome yellow (PbCr <sub>0.4</sub> S <sub>0.6</sub> O <sub>4</sub> )
	Undated Leaflet 5A	-	sigm. 450 <sup>a</sup> , 507 <sup>d</sup>	593, 624, (δ <sub>as</sub> SO <sub>4</sub> <sup>2-</sup> ), 830, 870, 900 (v <sub>as</sub> CrO <sub>4</sub> <sup>2-</sup> )	346, 380, 438, 843	-	[72, 5, 57]	Chrome yellow (PbCr <sub>0.4</sub> S <sub>0.6</sub> O <sub>4</sub> )
Orange	1847	Cl, Cr, Pb, Ca, S, (Fe)	sigm. 460 <sup>a</sup> , 540 <sup>i</sup> , 509 <sup>d</sup> and 555 <sup>d</sup>	601, 630 834, 861, 888	360, 378, 843	-	[81, 14, 56]	Chrome yellow (PbCr <sub>0.5</sub> S <sub>0.5</sub> O <sub>4</sub> ), undetermined orange pigment
	1855	Pb, Cr, Ca, S (Fe)	sigm. 530 <sup>a</sup> , 566 <sup>d</sup>	-	-	-	[69, 45.5, 40]	Minium
	1861	Pb, Cr, Ca, S, (Fe)	sigm. 530 <sup>a</sup> , 566 <sup>d</sup>	-	550	-	[62, 43, 39]	Minium
	1864	Ca, Pb, S, (Fe, Cr, Ba)	sigm. 530 <sup>a</sup> , 566 <sup>d</sup>	-	123, 550	-	[61, 43, 42]	Minium

	Undated Leaflet 5	Cr, Pb, Ca, S, (Fe)	sigm. 530 <sup>a</sup> , 574 <sup>d</sup>	-	123, 550	-	[63, 37.5, 45]	Minium
	Undated Leaflet 5A	-	sigm. 530 <sup>a</sup> , 570 <sup>d</sup>	-	123, 550	-	[63, 40.5, 45]	Minium
Red-orange	1847		sigm. 530 <sup>a</sup> , 600 <sup>i</sup>	-	254, 289, 346	-	[69, 40, 39]	Vermilion
Red-orange-1	1847		sigm. 530 <sup>a</sup> , 593 <sup>i</sup>	-	123, 550	-	[70, 46, 49]	Minium

Table 2. Summary of the material identification obtained for the four colours of the 1<sup>st</sup> chromatic circle: red, blue, yellow and orange hues (*a* = absorbance maximum, *r* = reflectance maximum, *i* = inflexion point, *sigm.* = form of sigmoid, *d* = first derivative maximum).

### 3.3. Colorimetric study

The typographic essay from 1847 differs from the other versions. Indeed, the yellow and blue colours are reversed (Figure 1e). The yellow and green hues also seem to be more represented than in the other versions at the expense of the orange hues (Figure 1). These last observations are visible in the *a\** and *b\** chromaticity diagram of the Figure 5 which represents each of the 72 hues of the circle from 1847, 1855, 1861 and 1864. Orange hues of the 1847 circle, under-represented in comparison with the more recent circles, are also more dispersed and create a discontinuity in the representation of the different hues (Figure 5a).

The Figure 5d shows that the results of the circle from 1864 are similar to those already obtained by F. Viénot in 2000 [21]: the chromaticity diagram of the 1864 circle is not perfectly circular and not centred around the white. The same results are observed in the first typographic essay from 1847 (Figure 5a), the circle from 1855 (Figure 5b) and the one from 1861 (Figure 5c). Several green, blue and yellow hues in the circle of 1847 overlap or own very closed *a\** and *b\** coordinates (Figure 5a). The Figure 5b shows that the contours of the 1855 circle are more circular. The distribution of blue, green and red hues is more linear, with the exception of the yellow and orange hues. Indeed, the distribution of the latter may be affected by the degradation described in part 3.2.2.3.4. The 1861 and 1864 versions show a clear difference in the blues, yellows and reds, which no longer overlap. It appears that the more recent the circle, the closer the distribution of the 72 colours is to a regular circular shape.

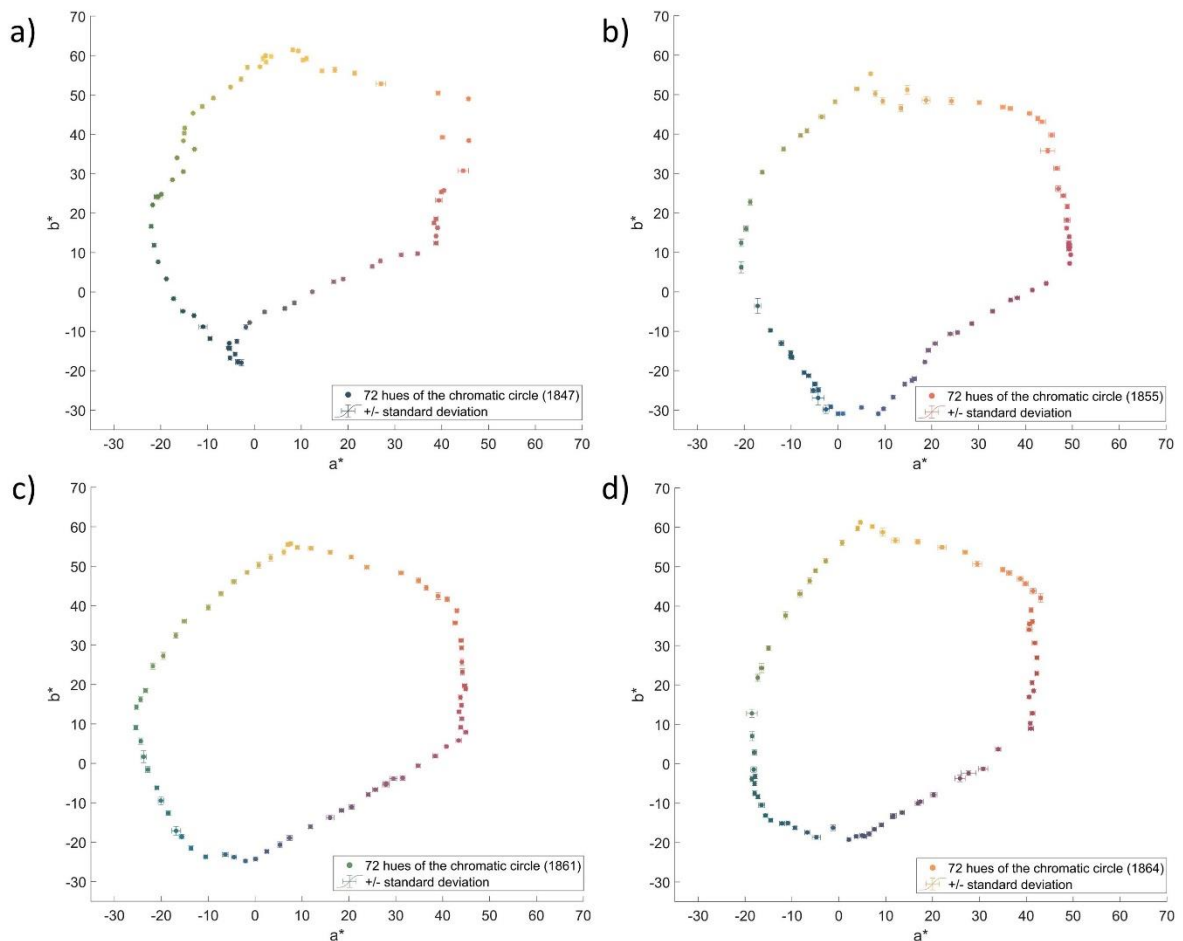


Figure 5.  $a^*$  and  $b^*$  chromaticity diagram of a) Typographic essay from 1847, b) 1<sup>st</sup> chromatic circle from 1855 [4], c) 1<sup>st</sup> chromatic circle from 1861 [5] and d) 1<sup>st</sup> chromatic circle from 1864 [6].

## Discussion

The full range of non-invasive techniques applied on a series of chromatic circles dated from 1847 to 1864 reveals a material and visual evolution through the different editions.

The printing technique used for the circle from 1847 has a particular impact on the visual representation of the circle. Indeed, material analysis has shown that two adjacent colours on the circle can be printed with two different inks, *i.e.* presenting different chemical composition. The red-orange hue was printed with a HgS-based ink, the next red-orange-1 hue with  $Pb_3O_4$ , and finally the “pure” red hue was a mixture of cochineal lake and HgS. These results may explain the less homogeneous visual appearance of this circle and the gaps between certain red-orange hues in the  $a^*$ ,  $b^*$  chromaticity diagram. After the first typographic essay from 1847, circles were printed using the technique entitled chromochalcography. This technique is based on the use of 4 superimposed inks of different thicknesses to obtain the 72 colours of the circle. The ink’s thickness is thus controlled by the engraving depth of the steel plate. The chromaticity diagram in the Figure 5a-d revealed an improvement of the hue gradient through the four editions. It is particularly visible for the red hues along the  $b^*$  axis. In the latest versions from 1861 and 1864, the transition from one hue to another is more linear while the red ink composition remains unchanged, highlighting an improvement of the

printing technique. The thicknesses of inks applied were probably more controlled thanks to the accumulated experience in printing the latest editions from 1861 and 1864.

The material analysis of the various colour circles shows a slight evolution in the chemical composition of the inks used for printing. These changes could be the consequence of the product availability or printers' preferences, but one cannot exclude the role of E. Chevreul and R. Digeon in making informed decision. The red ink was composed of a mixture of vermilion and cochineal lake in the first typographic essay from 1847, whereas eight years later, vermilion was abandoned in favour of the sole cochineal lake. This evolution may be justified by E. Chevreul's desire to avoid mixing organic and inorganic materials to ensure the longevity of his circles. Indeed, he wrote in his book: "above all, it was necessary to ensure the base of each colour and not to mix mineral substances with vegetable or animal substances" [36]. The composition of orange inks presents little changes over the editions. The typographic essay differs with a mixture of chrome yellow and undetermined orange pigments soon replaced by a minium-based ink in the following editions. Another subtler evolution exists in the case of the yellow inks. The Cr/S ratio of the lead chromate changed between the different editions from 1847 to 1864. This ratio depends entirely on the synthesis conditions and its modification is known to have an impact on the hue [27]. Thus, the lower the proportion of S, the more orange the pigment. This trend is clearly observed between the version from 1847 ( $\text{PbCr}_{0.5}\text{S}_{0.5}\text{O}_4$ ) and 1864 ( $\text{PbCr}_{0.7}\text{S}_{0.3}\text{O}_4$ ), for which the proportion of red represented by  $a^*$  in the yellow hues increases from -5 to 7 respectively. The baryte filler added in the yellow ink from 1864 may have been used to correct and lighten the yellow tint, which reaches values of around 60 in  $b^*$ , similar to those of 1847. With the higher ratio in sulphur, the chrome yellow-based ink of the editions from 1855 and 1861 are supposed to be the most yellow in tint. However, a decrease from 60 to 50 in  $b^*$  for the yellow and an increase at around 8 in  $a^*$  for the red have been observed. These results could be explained by the higher proportion of S that have certainly led to a darkening of the orange ink, as observed in the edition dated from 1855. Finally, Prussian blue is used in the editions from 1847, 1855, 1861 and leaflet 5A, while a mixture of Prussian blue and green copper arsenate is characterized in the leaflet 5 and in the last version from 1864. A correlation can be established between the new choice of materials and the hue represented on the circle. The blue ones from the 1855 circle made of Prussian blue achieved a number of -30 in  $b^*$  while the ones of 1864 circle do not exceed -20. The addition of a copper-based green pigment obviously modified the colour but also allow to increase the number of blue-green hues in the region -20 in  $a^*$  and -10 to 0 in  $b^*$  (Figure 5b, c). The edition from 1864 is then characterized by a greater change in the materials that compose the ink. This could be the result of a change of printer since the name of "Lamoureux imp." is added at the bottom of those late colour plates.

## 4. Conclusion

A combination of colorimetric and material analyses has been proposed to study a major 19<sup>th</sup>-century colour classification system. These light sensitive and precious graphic arts required the complementary uses of several non-invasive analyses. The combined VNIR-RIS, FORS-SWIR, XRF, mid-FTIR and Raman spectroscopies allowed to deeply characterize the paper support and the inks' composition, and to provide an overview of their conservation state. This material identification revealed the coexistence of vermilion, minium, cochineal lake and lead chromate, Prussian blue or Emerald/Scheele green, which fit perfectly into the context of the colour revolution. More particularly, the synthesis of the Prussian blue was discovered in the early 18<sup>th</sup>-century, the copper arsenate pigment in the end of 18<sup>th</sup>-early 19<sup>th</sup> century, while lead chromate yellow was synthesized in 1804 by Nicolas Vauquelin, one of E. Chevreul's teachers [41]. On the other hand, cochineal lake and minium,



the red and orange inks respectively, had a long history of use and were preferred to other new pigments such as the chrome orange ( $\text{Pb}_2\text{CrO}_5$ ) [41].

Furthermore, the joint study of several printed editions: 1847, 1855, 1861 and 1864 revealed a technological evolution that led to an improved colour representation through time. The 1847 typographic essay stands out by its different printing technique and inverted colour representation. The latest editions dated from 1855, 1861, 1864 and the two free leaflets 5, 5A were printed by chromochalcography. The digital microscope observations and the description in E. Chevreul's book revealed that this technique appears to be similar to the aquatint. The colorimetric study highlighted the improvement of the printing technique between the 1855, 1861 and 1864 versions, resulting in an enhanced visual continuity from one colour to the next. Moreover, the material study revealed a slight change in the composition of the inks through time, which also affected the visual representation of the circle. The last version from 1864, particularly stands out from the others, probably because of a change of printer. The Prussian blue ink of the version of 1847, 1855 and 1861 is replaced by a mixture of Prussian blue with a copper-based green pigment, and similarly a barium filler appeared for the yellow ink. Despite the change of printer, the continuity and improvement in colour representation was assured. This legacy can be explained by the fact that R. Digeon still appears as the engraver of the steel plates and could have transmitted its practical knowledge to the new printer. The visual appearance of these circles is therefore the result of the choice of print and materials, as well as the effects of time on the pigments and paper. The state of preservation of these circles may have varied according to the environmental conditions of their storage location and their personal history (longer exposure to light, variation in temperature or humidity). Opening this study to a larger number of books per edition will provide a better overview of the variability of printing within the same edition, and of their state of preservation.

This study shows that E. Chevreul's chromatic circles are witnesses of the chemical and technical innovations in the colour field during this period. In the future, new material and colorimetric studies could be carried out to better understand the influence of these different colour representation systems on their contemporary artists.

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## Supplementary materials

### A. Calculation to convert a reflectance spectrum into CIELAB coordinates

The tri-stimulus X, Y and Z are calculated for each pixel as the integral of the reflectance spectrum of this pixel, the wavelength-dependent spectral power constant is defined by the choice of the illuminant and the corresponding observer function  $\bar{x}$ ,  $\bar{y}$  or  $\bar{z}$ <sup>1</sup>. This last one defines the wavelength sensitivity of the algorithm. Like the standard observers are near to zero at wavelength lower than 380 nm and greater than 700 nm, all the data outside this range have a negligible impact on the coordinates X, Y and Z.

$$X = 100 \cdot \frac{\int_{\lambda_{min}}^{\lambda_{max}} I(\lambda)R(\lambda)\bar{x}(\lambda)d(\lambda)}{\int_{\lambda_{min}}^{\lambda_{max}} I(\lambda)\bar{y}(\lambda)d(\lambda)}$$

$$Y = 100 \cdot \frac{\int_{\lambda_{min}}^{\lambda_{max}} I(\lambda)R(\lambda)\bar{y}(\lambda)d(\lambda)}{\int_{\lambda_{min}}^{\lambda_{max}} I(\lambda)\bar{y}(\lambda)d(\lambda)}$$

$$Z = 100 \cdot \frac{\int_{\lambda_{min}}^{\lambda_{max}} I(\lambda)R(\lambda)\bar{z}(\lambda)d(\lambda)}{\int_{\lambda_{min}}^{\lambda_{max}} I(\lambda)\bar{y}(\lambda)d(\lambda)}$$

The L\*, a\* and b\* coordinates are calculated from the X, Y and Z values with the following equation.

$$L^* = 903,3 \left(\frac{Y}{Y_0}\right) \text{ for } \frac{Y}{Y_0} \leq 0,008856$$

$$L^* = 116\left(\frac{Y}{Y_0}\right)^{\frac{1}{3}} - 16 \text{ for } \frac{Y}{Y_0} > 0,008856$$

$$a^* = 500 \left[ f\left(\frac{X}{X_0}\right) - f\left(\frac{Y}{Y_0}\right) \right]$$

$$b^* = 200 \left[ f\left(\frac{Y}{Y_0}\right) - f\left(\frac{Z}{Z_0}\right) \right]$$

$$f(x) = x^{\frac{1}{3}} \text{ for } x > 0,008856$$

$$f(x) = 7,787x + \frac{16}{116} \text{ for } x \leq 0,008856$$

X<sub>0</sub>, Y<sub>0</sub> and Z<sub>0</sub> have respectively these values: 94.81, 100 and 107.34 for the illuminant D65 and observer 10°.

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<sup>1</sup> R. S. Berns, Color science and the visual arts - A guide for conservators, curators, and the curious, Getty publications. 2016.

Figure B. Microscope digital observations with ©Dinolite: a) orange hue, b) zoom on the degraded part of the orange hue c) yellow-green hue and d) zoom on the yellow-green hue of the 1<sup>st</sup> chromatic circle from 1855 (ref. V-4527, BnF)

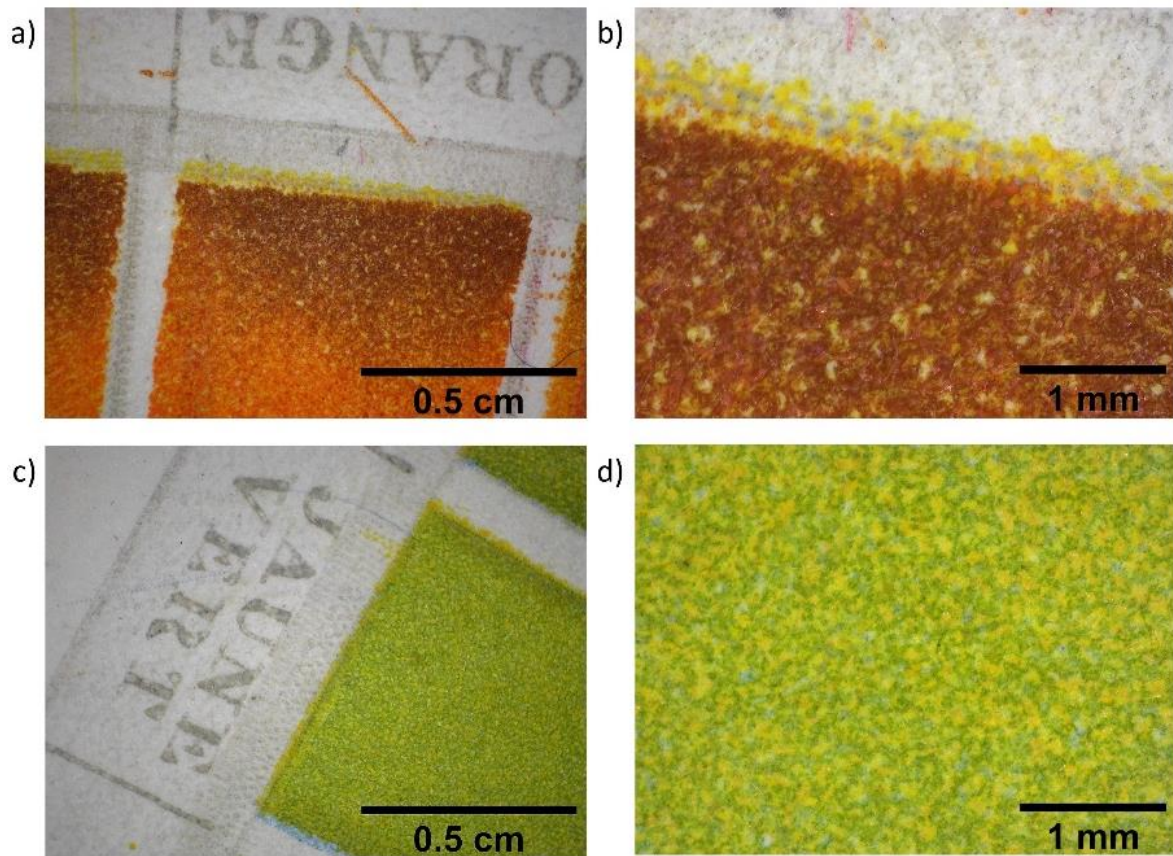


Figure C. Comparison of visible reflectance spectra of a) the orange-yellow and b) orange hues on the degraded and non-degraded areas of the 1<sup>st</sup> chromatic circle from 1855 (ref. V-4527, BnF)

