

# James Ensor's pigment use: artistic and material evolution studied by means of Portable X-Ray Fluorescence Spectrometry

Geert Van der Snickt<sup>a\*</sup>, Koen Janssens<sup>a</sup>, Olivier Schalm<sup>a</sup>, Cristina Aibéo<sup>b</sup>, Hauke Kloust<sup>c</sup> and Matthias Alfeld<sup>a,c</sup>

<sup>a</sup> University of Antwerp, Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium.

<sup>b</sup> Università di Firenze, Dipartimento di Chimica, Via della Lastruccia 13, 50019 Sesto Fiorentino, Italy.

<sup>c</sup> Universität Hamburg, Department of chemistry, Martin-Luther-King Platz 6 20146 Hamburg, Germany.

\* Correspondence to: Geert Van der Snickt, University of Antwerp, Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium. geert.vandersnickt@ua.ac.be, Tel: +32 3 820 23 63, fax: +32 3 820 23 76.

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## Abstract

*In this paper, Portable X-Ray Spectrometry (PXRF) was employed as a screening tool for determining and comparing the pigment use in a large series of paintings by the Belgian artist James Ensor (1860-1949). Benefits and drawbacks of PXRF as a method, and the applied set-up, are discussed from a practical, conservational and instrumental perspective. Regardless several restrictions due to the set-up and/or the analytical method, it appeared feasible to document the evolution with time several modifications in Ensor's use of inorganic pigments and to correlate this technical evolution with stylistic developments. Nevertheless, it became clear that a full identification of all materials present can only be done by means of the analysis of (cross-sectioned) samples.*

## 1. Introduction

In this work, a series of paintings by the painter and etcher James Ensor (1860-1949) were analysed in situ (i.e. in the museum or gallery where they are normally on display) by means of a Portable X-Ray Fluorescence (PXRF) spectrometer. The paintings belong to the collection of several Belgian and Dutch museums and private institutions and represent all aspects of the intriguing painted oeuvre of this Belgian avant-garde artist.

The work described here is part of a larger project aimed at a systematic study of the use of pigments in the 19<sup>th</sup>-C. The paintings from this period constitute an interesting field of research from an analytical chemistry point of view. The expanding chemical knowledge lead to the development of numerous new synthetic pigments and dyes in this period. Some of these new pigments were more colourful than the older pigments and therefore gradually replaced them. Others were just a synthetic equivalent for naturally occurring pigments, with a similar but purer and more homogeneous composition. However, nowadays it becomes clear that not all of these 'modern' pigments are as permanent as expected. This is for instance the case for cadmium yellow (CdS), which fades due to oxidation to semi-transparent/colourless CdSO<sub>4</sub> and flakes [1]. Consequently, it is of great importance for conservators to know which pigments are present in their collection of paintings. Based on this knowledge, they are able to trace degradation processes in an early stage and consider adapted conservation conditions and/or treatments.

A second motive for the study of 19<sup>th</sup>-C pigments is related to dating and authentication of paintings. The occurrence of a synthetic pigment in a painting is often employed to question the genuineness of the work of art. In such a case, conservators usually verify whether there is a

discrepancy between the assumed date of the painting and the date of invention or introduction of the pigments present. In spite of the relevance of this so called 'palette anachronism', the discrepancy between the date of invention and the exact moment when artists actually start to introduce these modern pigments in their paintings has not yet been investigated systematically.

Finally, 19th-C paintings have been analysed in the past in a rather sporadic way, e.g. in the framework of the conservation treatment of one particular work of art. However, the lack of a general frame of reference for this period often prevented researchers to compare or estimate their findings: are the identified pigments (a)typical for a certain period or school? Are there geographic differences? Do progressive painters have a preference for using innovative pigments or not? Does the availability of new pigments influence their painting style or vice versa?

### **The Oeuvre of James Sydney Ensor**

Ensor, who lived in the second half of the 19th- and the beginning of the 20th-Century, is generally considered to be one of the most important Belgian artists of that period. He affected many of his contemporaries and his influence is perceptible in the work of numerous subsequent artists (such as Paul Klee, Emile Nolde, Marc Chagall, the Cobra group, Jan Toorop, etc.), until deep in the 20th-C [2]. As a result, Ensor's oeuvre is exhibited worldwide on a regular basis (e.g. the Museum of Modern Art in New York is planning a retrospective in 2009). The fruits of his long and productive career, his self-obsessed personality and his life are the subject of continuous, intensive study by art historians, conservators, historians and even psychologists [1-3]. Apart from its relevancy and its volume, Ensor's oeuvre was also selected for a rather practical reason as a large part of his paintings is currently located in the Benelux. Therefore, his work was easily accessible from a geographical point of view.

From a stylistic point of view, the oeuvre of James Ensor is usually divided into three periods: (1) a sombre, realistic period (1875-1885), (2) a grotesque, symbolist period (1885- ca. 1900), and (3) a luministic period (ca. 1900-1949). The first period starts in 1875, and is characterised by an impressionistic technique. Real-life settings were painted in a suggestive way by building up volumes with thick patches of paint next and over each other. The colours are mostly sombre and tempered, with the exception of some highlights to achieve a claire-obscur effect. From 1885 on, Ensor developed a personal, metaphorical style and language, dominated by masks, skulls, scatology, death and hideous caricatures [2]. As a result, Ensor's painting style abruptly transformed from realism with a sombre tonality to symbolic compositions with bright and pure colours. The period from 1880 to ca. 1900 is therefore considered as his most creative. By the turn of the century, Ensor had become a well-respected artist, and this in spite of the explicit stinging criticism in his work, aiming at all layers of society. However, the acknowledgement of his work by society was accompanied by the fading of his creative power. Around 1900, Ensor evolved towards a luministic, post-impressionistic style with a repetitive and rather decorative character. The paintings of this period, are typified by thin paint layers revealing parts of the preparation layers, and a monotonous, pale colour scheme of pink, yellow, white, green and blue. Nevertheless, he kept working until he died at the age of 89, as a renowned eccentric.



*Fig. 1: (A) The PXRf instrument mounted on a studio camera stand during analysis of 'The lady eating oysters' (1882) in the Museum of Fine Arts, Antwerp, Belgium; (B) The PXRf installed on a lighter tripod during analysis in the depot of the Royal Museums of Fine Arts Brussels; (C) the relatively large analysis spot of ca. 1 cm<sup>2</sup> can render the analysis of small sized paintings and/or finely painted compositions with small colour areas difficult.*

## 2. Experimental

For this systematic study, the TRACeR III-V PXRF instrument from Keymaster Technologies (currently Bruker) was employed. Primary X-rays are generated by a Rh-tube with a maximal acceleration voltage of 40 keV and a beam current of 2 to 25  $\mu\text{A}$ . The irradiated spot has a circular shape with a surface of approximately 1  $\text{cm}^2$ . Spectra were collected by means of a peltier cooled SiPIN diode detector with a resolution  $\sim 175\text{eV}$  at 5.9 KeV. Detector and source are orientated in a  $45^\circ$  geometry. Before impinging on the object, the X-rays pass through a small chamber which can be evacuated by means of an external pump. However, this last option, which slightly reduces the air-path for the primary and fluoresced X-rays, was not employed during these measurements described here. In addition, this chamber is provided with an air-locked port which can be used to insert metallic filters in the beam path (e.g. an Al/Ti filter supplied by the manufacturer). All measurements were performed without filter, at a voltage of 40 keV, a current of 2.3  $\mu\text{A}$  and an acquisition time of 200s (live time). The resulting spectra were evaluated using the software package AXIL [4].

This compact instrument can be operated autonomously by means of a clip-on PDA or alternatively through a (portable) computer, via a USB connection. The PXRF device can be powered by electric mains, or by means of a rechargeable battery with a life span of 3-4 hours. Ease of use and safety are important issues when fragile art objects are involved. Therefore, the cable-less mode with PDA and battery contributes significantly to the aptness of this instrument in most situations. The absence of cables permits free handheld use; however, more stable and reproducible positioning of the instrument is required. For this reason, the apparatus was mounted on a solid studio camera stand (see Fig. 1A) permitting controlled and accurate movement of the device along the X-Y-Z axes. When mounted in this manner, the device could be levered safely to the desired position, leaving a few mm between its tip and the object. When no studio camera stand was on hand, a lighter and easy-transportable, yet less easily adjustable tripod was used, as illustrated by Fig. 1B. In this case the entire set-up first had to be moved across the floor to the desired lateral position along the X-axis, then the instrument could be winched to the desired height (Y-axis) and distance (Z-axis).

### Detection Limits

Detection limits were determined by analysing a disk of NIST SRM 612 standard glass at 40 keV for 1000s (live time). The resulting spectra were evaluated with the software package AXIL in order to determine the net peak areas and the background signal for all elements [4]. The detection limit values shown in Fig. 2 were derived by employing the formula:

$$C_{MDL} = C_{sample} \cdot \frac{3 \cdot (\sqrt{I_{background}})}{I_{signal}}$$

With  $C_{MDL}$  as the Minimum Detection Limit (MDL, in ppm),  $C_{sample}$  as the concentration of the element in the standard,  $I_{background}$  as the integral of the background and  $I_{signal}$  as the integral of the net fluorescence signal. The non-certified concentration values of NIST SRM 612 were taken from N.J.G. Pearce, et al [5] and from the webpage of the Max Planck Institut Mainz [6]. As fig. 2 demonstrates, optimal measuring conditions correspond to MDLs in the range 1-10 ppm for most elements of interest when a spectrum collection time of 1000s is employed. However, in the field, various circumstances such as surface effects and heterogeneity of the paint, limited measuring times, a larger distance between sample and detector, etc. can have a negative effect on the MDLs.

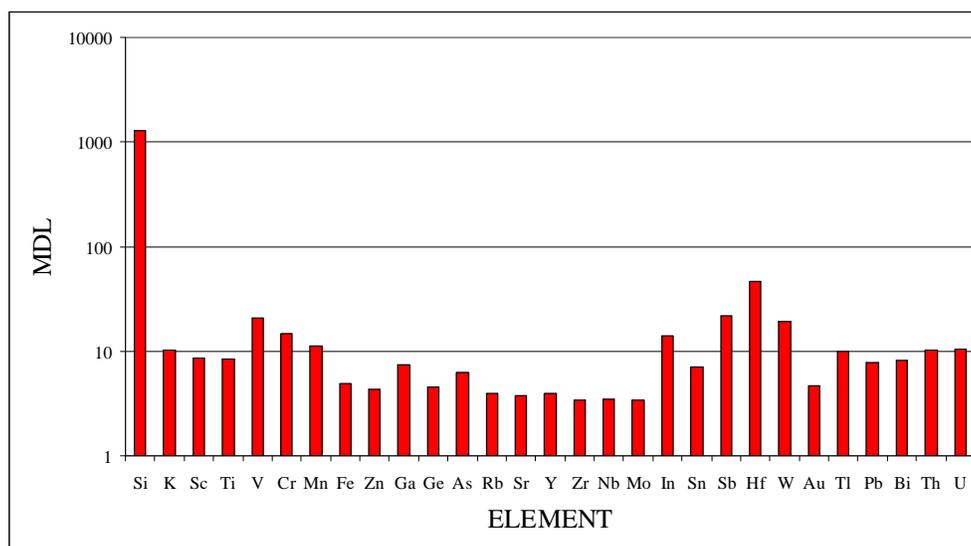


Fig. 2: Minimum detection limits in ppm of the TRACeR III-V from Keymaster Technologies. Measurements performed on a NIST standard 612 at 40 keV, live time 1000s.

### 3. Results and Discussion

#### Set-up

At the beginning of this project, it became clear that the main advantages of PXRF are its flexibility and “admissibility”. As this instrument can be brought to the location of the painting, it is not necessary to sample or to transport precious and fragile works of art to a laboratory. The device was mounted in situ on a camera stand or tripod so the measurements could be performed directly on the object, without the need of touching or preparing the surface. As a result, even the manipulation intra muros and the related labour cost of museum staff remained limited. In fact, an intervention of technical personal was only required in case the painting was shielded by a protective cover (e.g. climaboxes) or when the painting was kept in tightly spaced depot racks. In the latter situation, the painting had to be moved from the depot cupboards to a nearby easel. In general, the PXRF could be positioned in the X-Y-Z directions in an accurate and safe way, without the risk of touching the painting.

Since no mechanical contact with the analysed surface is required and thanks to the low-cost, low-risk and non-destructive aspect of this type of analysis, all curators and conservators that took part in this study were happy to lend their cooperation to this research project. In this way, it became feasible to carry out a substantial amount of measurements on a relatively large group of paintings in a relatively short time. Although the different analytical sessions were spread over three years, 50 paintings could be analysed in a total of ca. 10 working days. Figure 3 illustrates how these paintings were distributed over Ensor’s stylistic periods. As the graph demonstrates, most analysed paintings were situated in Period 1, while the paintings from the third period are somewhat underrepresented. This is due to the fact that Ensor’s most creative phase is situated in period 1 and 2, as explained in the introduction. Therefore, buyers from public institutions were less interested in work from his third, luministic period. As a result, this type of paintings is now found in private and therefore less accessible collections.

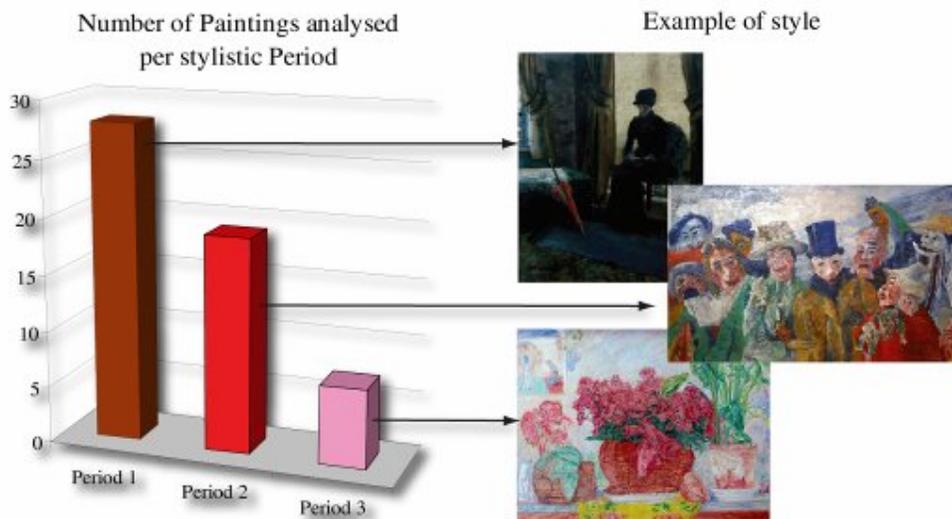


Fig. 3: left: graph showing the number of analysed paintings, per period. Right: typical examples illustrating the differences in style between the three periods.

### Analytical method

During the measurements, it became clear that the identification of the pigments was somewhat hampered by a number of limitations intrinsic to either the set-up or the analytical method. Being an element-specific technique, XRF is insensitive to the chemical state, crystal phase or molecular environment in which the detected elements are present. Therefore, it is well known that ensuing spectra need an interpretation by correlating the traced elements to visual information (e.g. colour of the analysed area) and a list of plausible pigments [7]. In most situations, this deduction enabled designating the pigments responsible for the visual colour. However, sometimes the result remained ambiguous. This was the case for the green areas in the paintings from period II and III where the recorded spectra displayed distinct copper and arsenic emission lines. However, at that time, two green pigments containing Cu and As were in use: Scheele's green ( $\text{Cu}(\text{AsO}_2)_2$ ) and emerald green ( $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$ ). In this specific case, XRF allowed to narrow down the number of plausible pigments to two, but was not specific enough to pinpoint the exact nature of the pigment.

Additionally, the penetrative property of the X-ray beam can impede a clear interpretation of the spectra in case of a set of superimposed paint layers. As the incident primary X-ray beam strikes the multilayered paint surface perpendicularly, the resulting spectra can include emission lines originally from several overlaying layers. In this situation, it sometimes remains unclear which element(s) can be assigned to the visible top layer. For similar reasons, the attribution of elements can be challenging in case of paint areas that were realised by means of mixtures of various pigments. A last drawback, which is related to this specific instrument instead of the PXR technique, is the relatively large dimensions of the analysed area (ca.  $1\text{cm}^2$ ). Consequently, the operator has to select homogeneous colour areas larger than  $1\text{cm}^2$ , in order to prevent interference from other pigments. This feature can be problematic in case of small and/or finely painted pictures, as shown in Fig. 1C. However the above mentioned limitations, were not considered as prohibitive: Ensor is known to employ relatively large colour areas. For most paintings, single paint layers were available, with paint often applied directly from the tube, only mixed with some white or dark pigment to modify the hue of the colour. As a result, for most analysed areas it was possible to determine the pigment, responsible for the main colour (green, red, blue, etc.).

Although this was not the case for all of his paintings, in general, Ensor's painting technique and pigment use appeared to be particularly well-suited for systematic analysis by PXRF.

Nevertheless, a combination of PXRF with other complementary techniques appeared necessary to obtain a more comprehensive understanding of the paint materials. Species-selective and/or spatial/stratigraphical information can be obtained via the analysis of (imbedded) samples with lab-based (e.g. Scanning Electron Microscope) or synchrotron radiation-based techniques (SR). Although recently a number of experimental, mobile set-ups have been designed for several spectroscopic techniques (e.g. micro-Raman Spectroscopy ( $\mu$ -RS), Fourier Transform Infra Red (FT-IR) and  $\mu$ -X-Ray Diffraction ( $\mu$ XRD)), most standard instrumentation is still lab-based and therefore requires sampling [8-10]. Additionally, synchrotron radiation-based methods (e.g. SR 3D  $\mu$ -XRF, SR  $\mu$ -XRD, SR  $\mu$ -X-Ray Absorption Spectrometry,  $\mu$ -tomography, etc.) are of particular interest for the study of paint samples. Various authors have recently demonstrated how the elevated spatial resolution, brightness and energy-selectivity of the primary beam renders SR techniques particularly well-suited for the characterisation of painting materials and their degradation phenomena [11-13]. Unfortunately, hitherto the access to synchrotron facilities for cultural heritage related research remains limited, effectively rendering systematic studies of large numbers of paint samples difficult.

## **Yellow**

During period I, Ensor applied predominantly Naples yellow to realise the yellow parts. This pale pigment was well fit to paint the soft yellow tones of his realistic stage (see Fig. 6) but the colour appeared too feeble to match his expressionist iconography of his second and third period. It seems that Ensor availed himself initially of chrome yellow to substitute Naples yellow, which disappeared completely from his palette after 1887. However, from 1896 on, he started to experiment with cadmium yellow and it appears that he abandoned chrome yellow around 1890. As a result, it is not unthinkable that Ensor would have decided to stick with the more stable cadmium yellow, after having put both pigments to test for some time. However, it seems that he never used both pigments in the same painting. This outcome illustrates how the artist was obliged to seek for innovative pigments in order to keep track with his stylistic transformation.

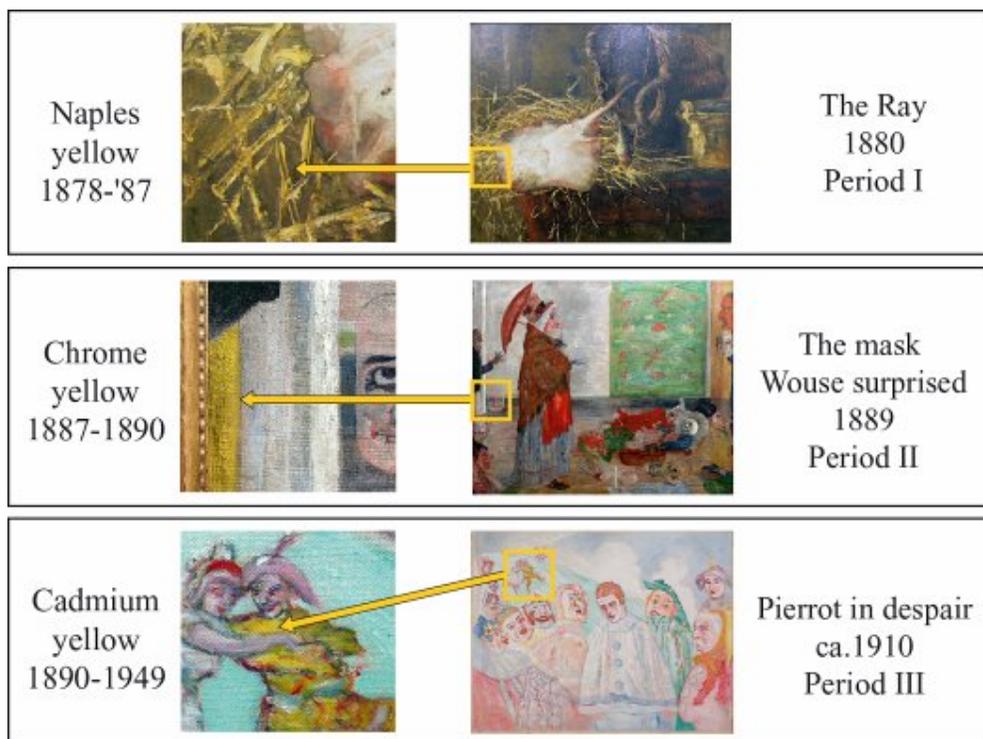


Fig. 4: The evolution of Ensor's yellow pigment, illustrated by examples from his three stylistic periods.

## Green

As Fig. 5 demonstrates, more than 75% of the green area's of Period I are characterised by a notable concentration of Fe and Cr, suggesting the use of a pigment composed by precipitating Prussian blue on a chrome based yellow. At that time, paint manufacturers supplied this composite, green pigment under various commercial names such as 'cinnabar green', 'chrome green', 'Brunswick green, etc. [14, 15]. According to the Pigment Compendium, this was one of most popular green pigments applied in protective and decorative coatings prior to 1940 [16]. In addition, this type of pigment was recently identified by Burnstock et al. [17] in paintings by Paul Cézanne (1839-1906). The remaining 25% revealed a combination of copper and arsenic, typical for either Scheele's green (copper arsenite) or the related emerald green (copper acetate arsenite). The latter poisonous compounds display a relatively vivid, green colour. As a result, it is not surprising that Ensor made extensive use of this type of pigments during his later and brighter phases: 44% of the greens in Period II and 67% during Period III. Only chrome was detected in the residual green paint areas of these periods, implying the presence of a chrome oxide or the more transparent hydrated form (viridian green).

Apart from that, a limited number of green paint patches seemed to contain exclusively iron, suggesting the employment of a green earth pigment or alternatively the combination of Prussian blue with a yellow earth pigment. Additional measurements on samples (e.g. Scanning Electron Microscopy, Raman Spectroscopy, etc.) would be necessary to clarify this matter.

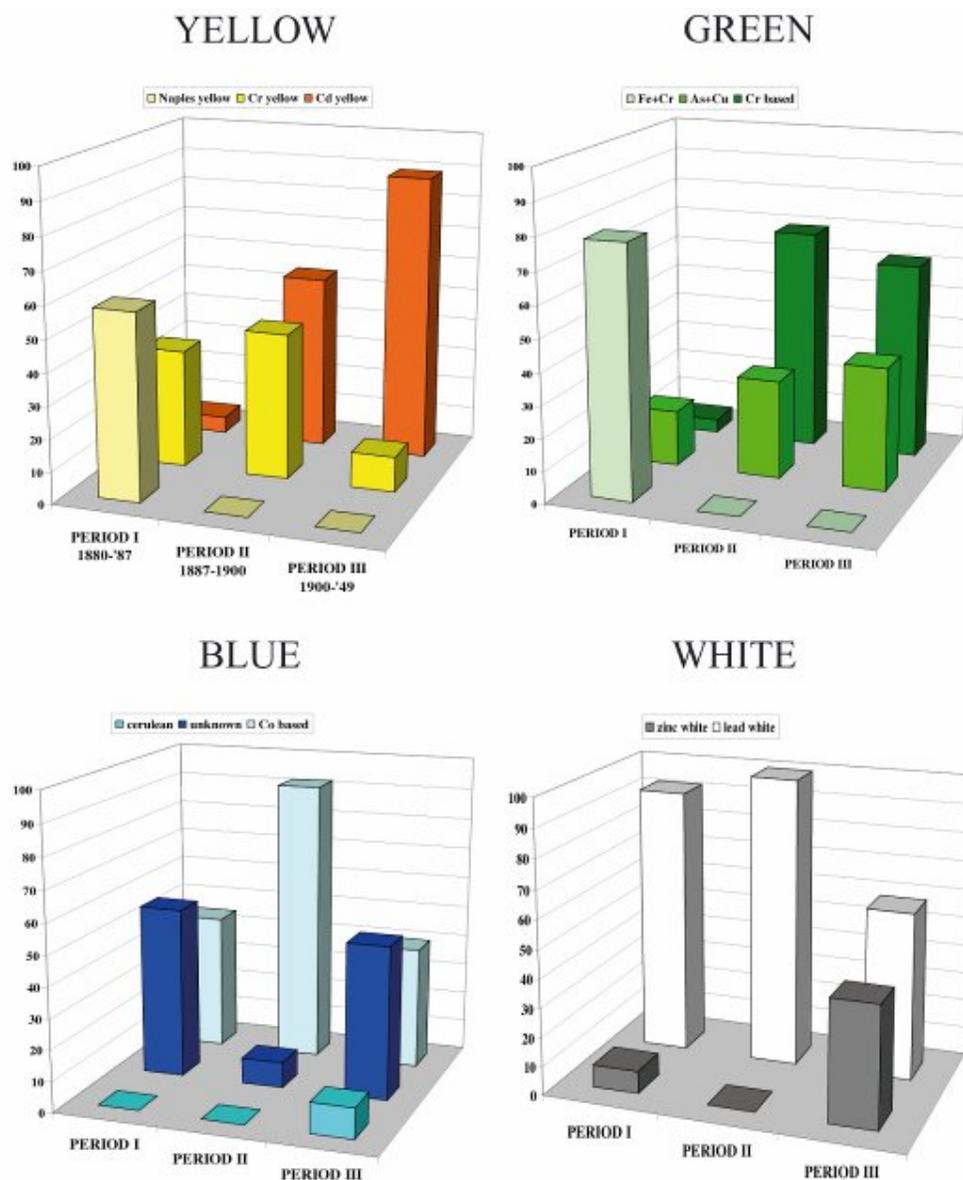


Fig. 5: Graphs presenting the pigments identified in Ensor's paintings, expressed as percentage per period

### White

One striking feature was the presence of substantial amounts of Pb and to a lesser extent of Ba and Ca in all spectra of all periods. The origin of the Pb, Ca and Ba could only be partially attributed to the variety of lead and calcium based materials used in paintings for different purposes (pigments, fillers, siccatives, ...). It is expected that the detected amount of lead is largely due to the presence of lead white. This lead carbonate was the only white pigment used in oil painting until the 19th-C. As a result, it has been intensively used by painters since Antiquity to realise white areas or to mix it with other pigments to lighten the colour. In addition, this pigment was used in preparation layers and it was commonly added to paint with the aim of counterbalancing the drawbacks of other pigments, e.g. to improve the drying properties or to opacify the paint. Nevertheless, it is

certain that Ensor applied a white, Pb-based pigment to produce the white colour in the paintings from the first period, as no other elements related to white pigments (Zn, Ba, Ti) could be observed in the white zones. This is considered as a noteworthy observation as zinc white, a less toxic alternative for lead based whites, was already commercialised since the first half of the 19<sup>th</sup> C. [14].

The same ambiguity exists with regards to the source of the observed calcium and barium compounds. Ca could be related to a chalk or gypsum-based ground layer, the use of chalk as a filler in paint, as a component of a pigment (e.g. a substrate for an organic dye, in bone black,...), etc. Barium was traced in a number of paintings, an element which is usually related to blanc fixe or lithopone. The latter are whitish/colourless painting materials often used as a neutral, low-cost filler in paints or preparation layers. Additional measurements on cross-sectioned samples would be necessary to clarify the chemical nature of Pb, Ca and Ba compounds observed and to situate these elements in the stratigraphy (ground layer, imprimatura, paint layers, etc.).

A last noteworthy finding was the occasional detection of Zn in several coloured areas. Zn is related to zinc white (ZnO) but, as mentioned above, Ensor used almost exclusively lead white during this period to produce white areas (see above). As a result, it was suspected that Ensor did not add zinc white deliberately to his palette, but that it was included in the paint tubes which he was known to purchase (e.g. from paint manufacturer Blockx). In conclusion, also the study of historic paint tubes forms an interesting topic for further research. As Fig. 7 demonstrates, by the turn of the century Ensor introduced zinc white to paint white zones. For most of these patches, the spectra revealed also intense Pb peaks. As a result, it remains unclear whether this lead content originated from an underlying preparation layer or if a mixture of zinc and lead white was used. The latter was common practice, as artists wanted to compensate for the poor drying and covering properties of zinc white [14].

### **Red and Pink**

Ensor clearly preferred the traditional pigment vermilion (HgS) to create the red colours, as Hg was found in all corresponding XRF spectra of all periods. The use of minium (Pb<sub>3</sub>O<sub>4</sub>), a red, lead based pigment, could not be confirmed, nor denied, as all spectra contained intense Pb-L emission lines (see 'white'). This pigment is not expected to be present as it was branded as a highly instable pigment by the paint manuals of that time [14]. In addition, the presence of any organic pigments could not be evidenced, as XRF is insensitive for this type of materials. Especially blue (indigo) and red (red lakes) precipitated colorants were in use at the end of the 19<sup>th</sup>-C. For instance, red lakes were often superimposed on vermilion-based layers to vary the reddish tone and/or to create depth.

In addition, a distinctive aspect of the third period is the abundant application of large surfaces (usually in the background) with a transparent, pink to bordeaux tints. This colour must have been obtained by an organic pigment (e.g. alizarine) as PXRF was unable to trace any inorganic elements in these areas.

### **Brown**

All ochre to brown tints were obtained by means of iron-based earth pigments, often in combination with vermilion to create a warmer shade. Apart from that, iron was traced in smaller intensities in numerous colour areas. This could indicate the use of elaborate mixtures of pigments, as it was customary to add green, yellow or brown earth pigments to the paint, in order to modify the tone of the colour. Also here, sampling would be necessary to unravel the nature of this kind of mixtures.

## Blue

Ensor was clearly keen on a cobalt based pigment, as he employed it in the paintings during all of his life. It would concern the modern cobalt blue or the instable and therefore less plausible smalt. However, for several paintings, the nature of the blue pigment was less obvious. The related spectra revealed, apart from the ubiquitous lead peaks, only relatively weak iron emission lines. The occurrence of this element did not allow to ascribe the iron content with certainty to Prussian blue: although, Prussian blue was a popular blue pigment during that period [14], the detected iron could also be due to an earth pigment mixed with another blue pigment or it could be situated below the blue paint. As a result, two other options remain plausible: (artificial) ultramarine or indigo. The first is exclusively composed of elements which are too light for ambient air XRF, where the second is organic. As a result, next to the demonstrated cobalt-based pigment, three other blue pigments remained plausible: Prussian blue, ultramarine or the organic indigo. It is remarkable that cerulean blue was detected in one painting of the third period, as demonstrated by Fig. 7.

## Black

Pure black pigments such as bone black or lamp black are rarely encountered in Ensor's painted oeuvre. Ensor seemed to favour mixtures of dark brown earth pigments (e.g. umber) with other colours to achieve the darker parts of his paintings. Nevertheless, a limited number of carbon black areas were located, sometimes typified by an elevated emission line of calcium. The latter points towards the employment of a bone or ivory black.

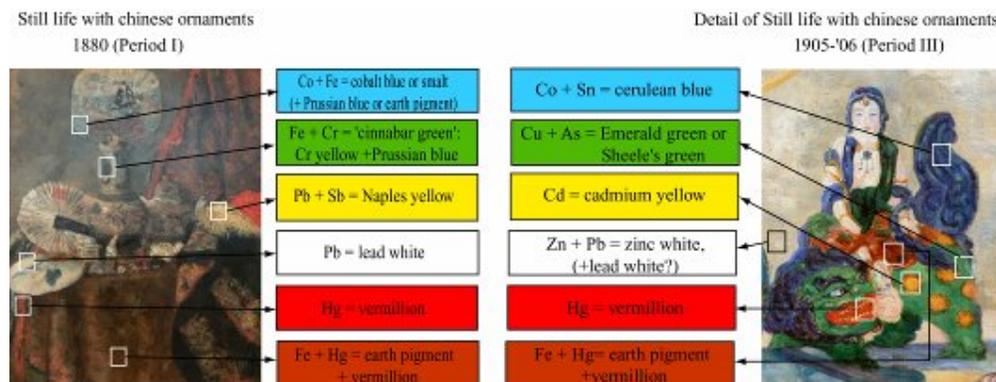


Fig. 6: The evolution in Ensor's use of pigments exemplified by a comparison of two paintings. Both works have the same theme (still life with Chinese ornaments) but date from different periods. The traditional green, yellow and blue pigments in the realistic still life of 1880 were replaced by brighter alternatives to realise the more vivid tonality of Ensor's late, symbolic oeuvre. In addition, zinc white replaces (partially) the toxic lead white.

date	name	museum	lead white	zinc white	vermilion	organic red	naples yellow	chrome yellow	cadmium yellow	Fe + Cr	Cu-As green	Cr based green	Co based blue	unknown blue	cerulean blue	brown earth
1880	The Lady on the breakwater	KMSKA	1							1				1		
1880	The Grey Sea	KMSKA	1		1		1			1				1		1
1880	the lady with the red sunshade	KMSKA	1		1		1			1			1	1		1
1880	a colourist	KMSKB			1			1		1						
1880	still life with chinese ornaments	KMSKB	1		1		1						1	1		1
1880	Still life with ray and hering	KMSKA	1		1		1			1	1					1
1880	still life with chinese ornaments	KMSKA	1		1		1	1		1			1			1
1880	still life with geraniums	KMSKA	1		1		1	1		1				1		1
1880	the cabbage	KMSKB	1		1		1	1		1						1
1880	the lamp boy	KMSKB	1		1									1		1
1881	the lady with the blue scarf	KMSKA	1		1		1			1			1	1		1
1881	the gloomy lady	KMSKB	1		1					1				1		1
1881	portrait of the father of the artist	KMSKB	1		1					1			1	1		1
1881	the lady in blue	KMSKB			1		1			1				1		1
1881	the bourgeois drawing room	KMSKA	1		1					1			1			1
1881	an afternoon in ostend	KMSKA	1	1	1					1						1
1882	the rendezvous	KMSKA			1					1	1			1		
1882	portrait of the mother of the artist	KMSKB	1		1		1						1			
1882	still life with oysters	KMSKA	1		1		1	1		1				1		
1882	the lady eating oysters	KMSKA	1		1			1					1			
1883	the rower	KMSKA	1		1									1		
1883	the drunkards	DEXIA	1							1			1	1		1
1883	the edge of the woods in Ostend	KMSKB	1										1			
1884	the white cloud	KMSKA	1	1							1			1		
1885	the lighthouse of Ostend	KMSKB	1							1				1		1
1887	carnival on the beach	KMSKB	1		1				1		1		1			
1887	adam and eve expelled	KMSKA	1		1			1					1			
	TOTAL PERIOD I		24	2	21	0	11	7	1	18	4	1	12	15	0	12
1889	the fall of the rebellious angels	KMSKA	1		1			1			1		1			1
1889	the theatre of masks	KMSKA	1		1			1			1	1				1
1889	the astonishment of Wouse	KMSKA	1		1			1			1		1			1
1890	the smacks	KMSKA	1		1					1	1					1
1890	the intrigue	KMSKA	1		1			1						1		
1890	still life with blue jug	KMM	1		1							1	1			
1891	mask and crustaceans	KMSKA	1		1								1			1
1892	the ray	KMSKB	1		1			1	1			1	1			
1892	flowers	KMSKB	1		1				1			1				
1896	flowers and vegetables	KMSKA	1		1	1			1			1	1			1
1896	flowers and chinese vases	KMSKB	1		1			1				1	1			1
1896	the painting skeleton	KMSKA	1		1	1			1			1	1			1
1896	shells	KMSKB			1								1			1
1896	hop frog's revenge	KMM	1		1				1			1	1			
1898	roofs of Ostend	KMSKA			1											
	TOTAL PERIODII		13	0	14	2	0	5	6	0	4	9	11	1	0	9
1902	the antique dealer	DEXIA	1	1	1			1			1	1	1			1
1906	still life with chinese ornaments	KMSKA	1	1	1	1			1		1	1			1	1
1909	flowers and blue vase	KMM	1	1	1				1			1	1			
1910	Pierrot in despair	KMM	1		1							1		1		
1914	la gamme d'amour	KMSKB			1					1	1	1		1		
1920	the azaleas	KMSKA	1	1	1	1			1		1	1	1	1		1
1925	the abduction of Andromeda	DEXIA	1		1							1		1		
1925	the fight	KMM			1				1			1	1			1
1939	skies	DEXIA	1	1	1				1		1	1	1			
	TOTAL PERIOD III		7	5	9	2	0	1	8	0	5	8	4	5	1	4

Fig. 7: Table with an overview of all pigments identified in Ensor's paintings.

## 4. Conclusions

PXRF in general and the Keymaster instrument specifically, allows accurate and controlled positioning of the device, proved to be suitable for studying a large amount of paintings. In addition, the non-destructive, low-cost and non-contact aspect of this technique allows to carry out a large number of measurements in a relatively short amount of time. In this way PXRF can be used for the analysis of paintings that are not involved in a conservation treatment as no samples need to be taken. The operation of this commercial device and interpretation of the results is relatively straightforward and accessible for conservators and museum staff. For the first time, a systematic and comparative study of groups of paintings becomes feasible. Nevertheless, analysis of cross-sectioned samples remains desirable to pinpoint the exact nature of all materials (including organic pigments) and to obtain stratigraphic information. The establishment of large databases of (inorganic) pigment occurrence becomes possible and is expected to open new prospects in the field of (technical) art history and painting conservation.

In spite of the fact that the limitations of the PXRF instrument did not allow for a full identification of all painting materials, the results demonstrated that the stylistic evolution of the artist involved a change in pigment usage. Ensor's shift towards modern materials appeared to coincide approximately with his stylistic developments. The technical limitations were either

related to the elemental nature of the method of analysis or to this specific instrument (large spot size). His early, impressionistic work (Period I: 1880-1887) with a gloomy, realistic iconography is dominated by the use of traditional pigments such as lead white, vermillion, Naples yellow, earth pigments, etc. Apart from these pigments, which have been in use since Antiquity, some modern materials were identified: a Ba-based filler, a compounded green containing iron and chrome, a cobalt-based blue, an unknown blue and sporadically a copper (acetate) arsenite and chrome yellow.

Ensor's realistic and tempered palette shifted towards a more aggressive and vivid tonality. During his symbolic phase (Period II: 1887-ca. 1900), Ensor suddenly started to apply sizeable colour areas with relatively pure pigments. This practice contrasted sharply with the painting technique of the first period, during which Ensor preferred to moderate the brightness of his shades (a) by intermixing darker pigments (e.g. earth pigments) with the paint and/or (b) by juxta- or superimposing darker paint strokes. The PXRF measurements suggest that Ensor realised this new and vibrant range of colours principally by employing the same assortment of pigments (vermillion, lead white, cobalt-based pigment, earth pigment, etc.) but in a different manner. This abrupt change was reflected in the analytical results by a simplification of the spectra. Apart from the major peaks caused by the most important colouring pigment, the spectra from the first period demonstrated a large variety of low-intensity emission lines (Fe, Hg, Co, etc.). In contrast, the second period spectra appeared to be less clouded by such minor peaks. Apparently, this stylistic progress also prompted Ensor to resort to modern yellow and green pigments: cadmium yellow and a chrome (hydrated) oxide were added to his palette. Also emerald green (or Scheele's green) and chrome yellow were abundantly used, two pigments which he experimented with during Period I, in a rather tentative way. This is probably due to the fact that Ensor's green and yellow pigments of the first period present relatively dark or pale colours. Ensor was possibly compelled to seek for alternatives, as it would have been hard or even impossible to enhance the brightness of these pigments, without causing a substantial diminishment in colour intensity.

Towards the turn of the century, Ensor evolved towards a luministic style (Period III: ca. 1900-1949), typified by thin paint layers and paler colours. What strikes the most in the paintings from this period is the introduction of zinc white, cerulean blue (occasional) and the abundant use of an organic pink/bordeaux pigment. Over the years, only two colours were painted with the same pigments in all three periods: the brown colour, using an earth pigment (+ vermillion) and red colour, using vermillion. Considering their date of invention, it can be concluded that Ensor introduced these new pigments relatively late (last decades of the 19<sup>th</sup>-C, first decades of 20<sup>th</sup>-C). However, it is not yet known whether this was due to geographical availability, to maintaining the academically imposed palette out of routine, or rather to a restraint towards non-established materials.

In the future, these results will be correlated with and supplemented by lab- and synchrotron-based analysis of (cross-sectioned) samples on the one hand and archival sources (e.g. order forms) on the other hand. In this way, this research will eventually lead to a complete overview of Ensor's use of pigments and is expected to supply a frame of reference for further research on 19<sup>th</sup>-20<sup>th</sup> C. paintings. From both a practical, deontological and economic viewpoint, this method made it feasible for the first time to carry out a systematic and comparative analytical study on a relatively large series of paintings.

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