In situ macro X-ray fluorescence (MA-XRF) scanning as a non-invasive tool to probe for subsurface modifications in paintings by PP Rubens

Reference:
van der Snickt Geert, Legrand Stijn, Slama Ina, Van Zuien Eva, Gruber Gerlinde, Van der Stighelen Katlijne, Klaassen Lizet, Oberthaler Elke, Janssens Koen.- In situ macro X-ray fluorescence (MA-XRF) scanning as a non-invasive tool to probe for subsurface modifications in paintings by PP Rubens
Microchemical journal - ISSN 0026-265X - 138(2018), p. 238-245
Full text (Publisher's DOI): https://doi.org/10.1016/J.MICROC.2018.01.019
To cite this reference: https://hdl.handle.net/10067/1515640151162165141

Accepted Manuscript

In situ macro X-ray fluorescence (MA-XRF) scanning as a non-invasive tool to probe for subsurface modifications in paintings by P.P. Rubens

Geert Van der Snickt, Stijn Legrand, Ina Slama, Eva Van Zuien, Gerlinde Gruber, Katlijne Van der Stighelen, Lizet Klaassen, Elke Oberthaler, Koen Janssens

PII: S0026-265X(17)30877-9
DOI: https://doi.org/10.1016/j.microc.2018.01.019
Reference: MICROC 3011

To appear in: *Microchemical Journal*

Received date: 3 September 2017
Revised date: 12 January 2018
Accepted date: 12 January 2018

Please cite this article as: Geert Van der Snickt, Stijn Legrand, Ina Slama, Eva Van Zuien, Gerlinde Gruber, Katlijne Van der Stighelen, Lizet Klaassen, Elke Oberthaler, Koen Janssens , In situ macro X-ray fluorescence (MA-XRF) scanning as a non-invasive tool to probe for subsurface modifications in paintings by P.P. Rubens. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Microc(2017), https://doi.org/10.1016/j.microc.2018.01.019

In situ Macro X-Ray Fluorescence (MA-XRF) scanning as a non-invasive tool to probe for subsurface modifications in paintings by P.P. Rubens

Geert Van der Snickt[1,2], Stijn Legrand[1], Ina Slama[3], Eva Van Zuien[4], Gerlinde Gruber[3], Katlijne Van der Stighelen[5], Lizet Klaassen[6], Elke Oberthaler[3] and Koen Janssens[1]

[1] University of Antwerp, Department of Chemistry, AXES research group, Groenenborgerlaan 171, B-2020 Antwerp, Belgium.
[2] University of Antwerp, Faculty of Design Sciences, Conservation Studies, Heritage and Sustainability research group, Blindestraat 9, B-2000 Antwerp, Belgium.
[3] Kunsthistorisches Museum Wien, Maria-Theresien-Platz, A-1010 Vienna, Austria.
[4] Independent conservator, Ribeslaan 91, NL-3053 ML Rotterdam, the Netherlands
[5] KU Leuven, Faculty of Arts, Art History, Blijde Inkomststraat 21, B-3000 Leuven, Belgium
[6] Koninklijk Museum voor Schone Kunsten Antwerpen, Leopold de Waelplaats 2, B-2000 Antwerp, Belgium

Abstract

Within the last decade, the established synchrotron- and laboratory-based micro-XRF scanning technology inspired the development of mobile instruments that allow performing in situ experiments on paintings on a macro scale. Since the development of the first mobile scanner at the start of this decade, this chemical imaging technique has brought new insights with respect to several iconic paintings, especially in cases when standard imaging techniques such as X-Ray Radiography (XRR) or Infrared Reflectography (IRR) yielded ambiguous results. The ability of scanning MA-XRF to visualize the distribution of elements detected at and below the paint surface renders this spectrometric method particularly helpful for studying painting techniques and revealing materials that remain hidden below the paint surface. The latter aspect is especially relevant for the technical study of works by Pieter Paul Rubens (1577-1640) as this highly productive seventeenth century master is particularly renowned for the continuous application of modifications during (and even after) the entire course of the creative process. In this work, the added value of MA-XRF scanning experiments for visualising these subsurface features is exemplified by interpreting the chemical images obtained on three of Rubens' key works. Special attention is given to three types of adjustments that are particularly relevant for the technical study of Rubens' oeuvre: (1) compositional changes ('pentimenti'), exemplified by results obtained on The Portrait of Hélène Fourment (ca. 1638), (2) extensions to the support ('Anstückungen'), illustrated by imaging experiments performed on the Venus Frigida (1614) and (3) Rubens' intriguing halos around flesh tones, as found amongst others in The Incredulity of Saint Thomas (1613). The ensuing insights in the paint stratigraphy and the underlying supporting structure illustrate the potential of MA-XRF scanning for the non-invasive, comparative study of Rubens' oeuvre. The results do not only augment the understanding of the complex genesis of Rubens' works of art and his efficient painting technique, but prove valuable during conservation treatments as well, as addressed in this paper.

Introduction

X-Ray Fluorescence (XRF) is an analytical technique that has been used for many decades in cultural heritage science. It is one of the most cited analytical techniques in literature, owing its popularity to the fact that it can detect a wide range of elements in a non-destructive, sensitive and efficient way [1, 2]. The dawn of commercial portable (PXRF) and handheld XRF devices (HHXRF) around the turn of the millennium entailed a substantial progress in the analysis of painted surfaces [3, 4], allowing to collect compositional data from a series of pre-selected spots of interest without the need of transporting or sampling the object under research. The development of a mobile Macro-XRF scanning instrument (MA-XRF) by Alfeld et al. at the beginning of this decade [5] now makes it possible to collect XRF spectra from the entire polychrome surface and presenting the ensuing compositional data in the form of images that are easier to interpret by heritage stakeholders than conventional analytical spectra and graphs.

The final result of a MA-XRF scanning experiment is a set of contrast images, each showing the distribution of a chemical element that can be related to one or more painting materials [6]. However, as MA-XRF is an elemental technique insensitive to the crystal structure or chemical environment of the detected elements, this assignment is not always unambiguous as identification is obtained through deduction, in particular by comparing the detected elements with an exhaustive list of painting materials and visual information such as the colour or morphology of the sample under study [7, 8]. By consequence, combining MA-XRF scanning experiments with more species-selective analytical information collected in situ and/or on cross-sections (e.g. XRD, Raman or FTIR spectroscopy) usually leads to a more comprehensive characterisation of the painting's constituents [9, 10]. The ensuing images are typically presented in black and white, with variations in grey scale between pixels expressing a relative difference in concentration of the elements detected.

Next to characterisation of the employed materials at the surface, the penetrative properties of the primary and secondary X-rays can be used beneficially to study a series of subsurface features such as overpainted compositions, pentimenti, covered paint losses, retouching and other physical changes [11, 12]. This is a particularly valuable aspect in heritage science as the objects under study often conceal a complex layer build-up, while a local accumulation of old interventions can render things even more complicated [13]. In those cases, MA-XRF imaging can look under the surface in a similar non-invasive way as X-Ray Radiography (XRR) and Infrared Reflectography (IRR) [14], two imaging techniques that are routinely deployed in museum galleries, but its element-specific aspect allows to look at the different materials and layers in a more selective way. Rubens vast oeuvre is well-suited to demonstrate this added value in view of his complex and variable modus operandi. In the past scholars have established that this seventeenth century master was liberated from established paint practices, an aspect that is reflected by a continuous experimenting during all stages of the conception of his paintings [15]. The resulting numerous adjustments were skilfully concealed by the master but nowadays are of interest to art historical scholars who are eager to unravel Rubens' creation process or to conservators for whom the understanding of the underlying structure and layer build up is vital to elaborate a suitable treatment strategy. However, the typical built-up of Western European seventeenth century paintings, often with thin paint layers that are rich in carbon- and iron- based pigments, not seldom limits the applicability of XRR and IRR imaging, while these materials appear favourable for MA-XRF scanning, as is discussed in the next few paragraphs. However, the discussion of the three case studies is limited to features that are most relevant for illustrating the potential of MA-XRF scanning as a full technical and art historical evaluation of the results would exceed the scope of this article.

Experimental

The paintings discussed in this paper were chemically imaged in reflection mode by means of a MA-XRF scanning instrument that was built by the AXES group of the University of Antwerp. This in-house device is an optimised variant of the setup described by Alfeld et al. as 'Instrument B' [5]. The measurement head consists of a compact 10W Rh anode transmission tube (Moxtek, UT, USA) operated at 45 kV and 200 µA and one Vortex EX-90 SDD detector with an active area of 50 mm² positioned in a 50° angle with respect to the incident X-ray beam. The diameter of the diverging primary beam was reduced by means of a 0.8-mm lead pinhole collimator. The XRF measurement head is mounted on a software controlled X-Y motor stage with a maximum travel range of 57 x 60 cm (h x v). MA-XRF scans were performed by sweeping the measuring head systematically over the paint surface. Careful positioning and alignment of the scanner ensures a stable distance of ca.1 cm in between the snout and the panel. Retaining this constant painting-instrument distance prevents fluctuation of the attenuation of the X-ray fluorescence signals in the ambient air. During the movement, XRF spectra were recorded every 700 µm (step size) with a dwell time of 200 ms (real time) for each spectrum (scan speed of c. 3.5 mm/s). The resulting spectral data cube was processed through dynamic analysis employing a combination of the Pymca [16], Datamuncher [17] and bAXIL [18] software packages. As the panel dimensions exceeded the travel range of the motors, each scene was divided into overlapping scan areas. After spectral deconvolution, the separate elemental distribution images of each panel were seamlessly compiled by means of the Datamuncher software. The greyscale of the resulting images is linear to the detected intensities. However, the levels in the histogram of each individual image were manually moved or stretched to optimize contrast and readability.

Results and Discussion

Compositional changes in the *Portrait of Hélène Fourment* – ca. 1638

Portrait of Hélène Fourment shows Rubens' second wife life-size and at full-length, merely wrapped in a fur coat. Although the spectator beholds the model portrayed in front of a neutral dark setting, Rubens scholars have always suspected an underlying, more animated background based on the topography of the paint surface that suggests underlying brushwork. Considered as one of the key works in Rubens' oeuvre, the panel painting has been studied intensively, hoping that the disclosure of hidden features would augment the prevailing view on its function and meaning. However, as illustrated in Figure 1, conventional XRR and IRR were not very informative on this aspect as the contrast in the radiography is dominated by a grid of supporting wooden beams on the reverse side of the panel (the 'cradle'), while the penetration of IR radiation is prevented by the infrared absorbing carbon black and earth pigments in the surface paint. The abundance of these pigments in the top layer is demonstrated by the MA-XRF maps of calcium (Ca-K) and iron (Fe-K), shown in Figure 1, respectively. The presence of earth pigments is monitored by plotting the distribution of the element iron that is indicative for its constituting hematite (Fe_2O_3) and/or goethite ($FeO(OH)$) crystals. The low energy fluorescence radiation emitted by the carbon atoms (0.28 keV) cannot be detected due to absorption by ambient air, but its distribution is indirectly revealed by the calcium content of the black pigment that is derived from bone or ivory ashes [19].

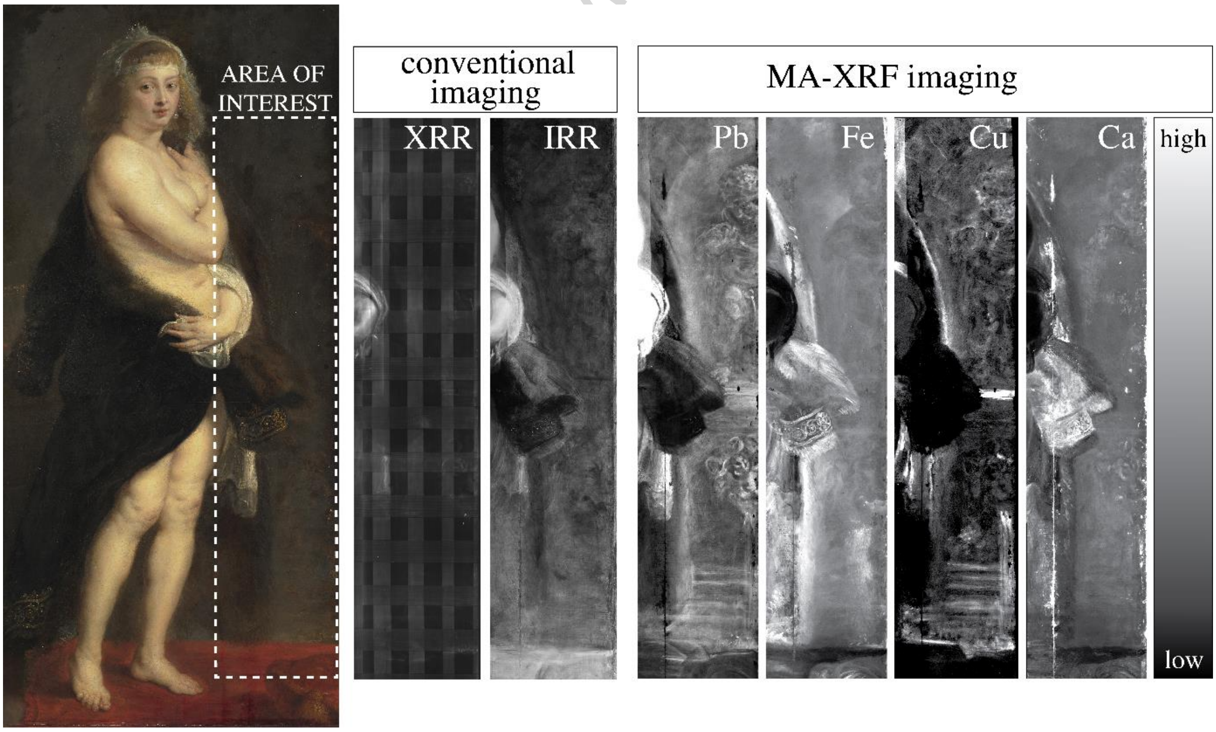

Figure 1: left: *Portrait of Hélène Fourment* by Peter Paul Rubens, 1638, inv. 688, Kunsthistorisches Museum, Vienna. The dotted white rectangle indicates the area that was imaged (Map size 1450 x 300 mm, step size 700 µm, 200 ms/pixel) Middle: the corresponding X-ray radiography (XRR) and infrared Reflectography (IRR) are not informative with respect to this hidden feature. Right: the corresponding MA-XRF maps of

Pb (0-11000 counts), Fe (0-10200 counts), Cu (0-4000 counts) and Ca (0-3700 counts), revealing an animated fountain below the dark surface paint.

In contrast, both interfering parameters are beneficial for MA-XRF scanning. Unlike IRR, the presence of carbon and iron containing materials renders the surface relatively transparent for X-ray radiation. As a result, these superimposed low Z elements have relatively low attenuating influence on the fluorescence radiation that is escaping from deeper inside the paint stratigraphy. In comparison with XRR, the separate MA-XRF images are not clouded by the underlying support. Although the vast mass of carbon atoms in the wooden beams is capable of scattering part of the primary beam, the wooden support and cradling do not show up in the elemental images as this artefact is eliminated from the MA-XRF maps by post-processing of the data set. Dedicated deconvolution software was developed and applied to allow for efficient and artefact-free extraction of net peak surfaces from the spectra [17, 18].

In this way, MA-XRF experiments revealed in great detail a fountain with a water-breathing lion's head and a peeing boy. As illustrated in Figure 1, the fountain is executed in lead(white), whereas water and shadows contain a copper pigment as well, most probably blue mineral azurite ($Cu_3(CO_3)_2(OH)_2$) or verditer, its synthetic equivalent. Outlines and details of the fountain can be vaguely distinguished in the iron and calcium distributions as well, suggesting that darker earth pigments and bone black were applied to create shadow effects. However, the contrast of these elements is levelled in the corresponding maps as the superimposed dark surface paint is containing the same elements, as mentioned earlier in this section. According to art historical scholars, the disclosed peeing boy or 'puer mingens' is a motif already known from Antiquity often referring to fertility or eroticism. In this way, the discovery confirms the suspicion that this was originally a private piece, intended only for the eyes of Rubens himself and his wife [20, 21].

Extensions to the support of *Venus Frigida* - 1614

Venus Frigida is an earlier work by Rubens showing Venus and Amor shivered with cold, accompanied by a satyr holding the horn of plenty, a scene referring to the classical proverb 'Without Bacchus and Ceres, Venus freezes' [15]. This sizeable work was selected to assess the potential of MA-XRF scanning for studying Rubens' peculiar studio practice of extending the support during and/or even after painting, in literature often referred to as 'Anstückungen' [22, 23]. At that time, it was customary that both the size of the support and the composition were defined prior to painting. The composition was usually well elaborated through an established process of successive preparatory drawings and paintings and a fitting panel or canvas (sometimes primed) was purchased ready-made from a panel maker [24]. During the execution of the painting, last minute compositional changes were kept within the boundaries of this support. Rubens however was one of the first to break free from this tradition, adding pieces of canvas or wooden boards without restraint during various stages of the creative process and this for a diversity of reasons [15]. Next to gaining insight in the genesis and original destination of Rubens's works, a thorough understanding of his compound supports also proves valuable during restoration treatments as the rather disordered execution can gives rise to conservation issues. For instance, for the *Venus Frigida*, the elemental maps in Figure 2 reveal distributions of various modern pigments lateral with the seams of both original as added planks that are typical for nineteenth to twentieth century retouching. The presence of Zn, Ba, Ti and Cr points towards industrial pigments such as zinc white (ZnO), barium sulphate ($BaSO_4$) or lithopone ($BaSO_4.ZnS$), titanium white (TiO_2) and assorted chrome-based compounds (chrome green, yellow or red) respectively.

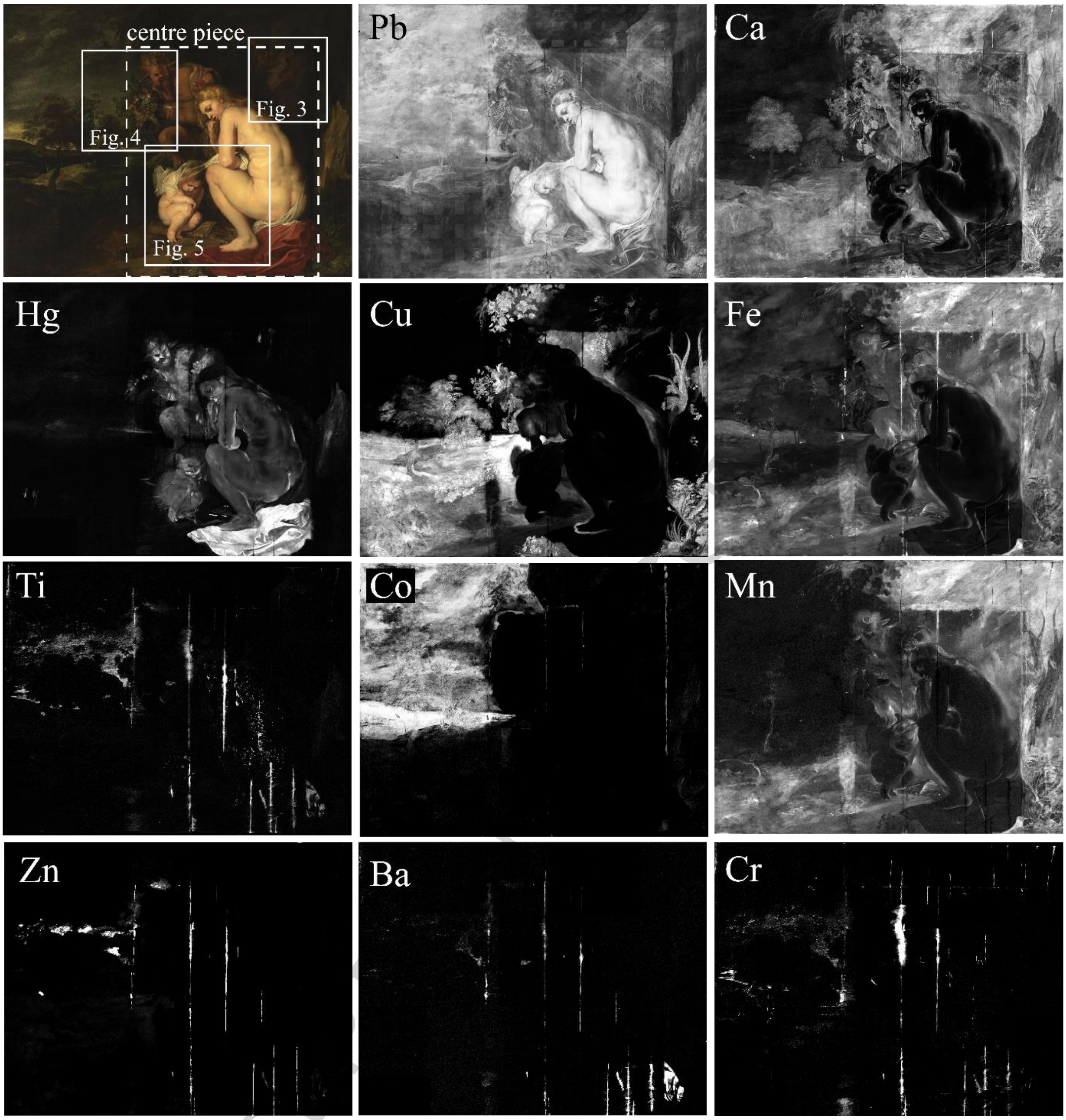

Figure 2: top left: *Venus Frigida* by P.P. Rubens, 1614, Royal Museum for Fine Arts Antwerp, inv. 709. © KMSKA - Lukas-Art in Flanders vzw. Photo Hugo Maertens. The dashed white rectangle indicates the original panel by Rubens while the surrounding landscape is a later extension. The white rectangles indicate detail areas shown in Figs 3 to 5. Other images: MA-XRF maps showing the distribution of Pb (0-7990 counts), Ca (0-6800 counts), Hg (0-3300 counts), Cu (0-1400 counts), Fe (0-7300 counts), Ti (0-1500 counts), Co (0-1000 counts), Mn (0-750 counts), Zn (0-10900 counts), Ba (0-480 counts) and Cr (0-1200 counts) over the entire surface of the panel painting (Map size 1450 x 1850 mm², step size 800 µm, 200 ms/pixel).

In the case of the Venus, it is believed that extensions were realised in two different stages and at least part was performed after Rubens' death [15], possibly with the aim to adapt the dimensions of the painting to an (architectural) setting (e.g. wainscoting) and/or a larger counterpart painting. The original panel painting was considerably smaller and vertically oriented, merely comprising the main figures, as indicated with a white, dotted rectangle in Figure 2. In a first phase, the panel was enlarged by adding four short boards on the top and one long board along the right flank. During close examination, conservators noticed that at the same time, a very narrow plank was attached to the left side as well. In a later stage, an expansive landscape was appended after attaching additional boards along the left side. The outlines of the 'centre piece' can be clearly distinguished in the distribution maps of lead and calcium. In particular, the lead distribution reveals Rubens' renowned streaky imprimatur, a monochrome, lead white containing layer that was applied prior to painting on top of the calcium-based preparation, toning down its white colour and at the same time providing a middle tone that allowed the artist to work more efficiently as only shadows and highlights had to be applied [25]. The detail scan in Figure 3 illustrates this aspect more clearly, giving evidence of an imprimatur in the centre piece that was applied swiftly and freely with a stiff brush. The coarse brush strokes emerge clearly in the lead and calcium images, running diagonally from top left to bottom right.

A striking feature, observed in other autograph works by Rubens as well, are the distinctive drippings just above Venus' back, signalling that the paint of the imprimatur was very fluid when applied. Both the texture of the brush strokes and the drips show up in negative in the calcium image, implying that the detected calcium fluorescence originates from the underlying chalk-based priming, with the low energy calcium signal attenuated where the overlying lead-based imprimatur is sufficiently thick. In certain small areas of the painting, these drippings can be seen by the eye but they emerge more prominent and comprehensive in the MA-XRF maps. The visualisation of these drippings, uncorrected by the master, exposes Rubens' efficient and unbound studio practice and his focus on obtaining an overall optical effect, to be experienced from a distance, rather than obtaining an immaculate paint layer.

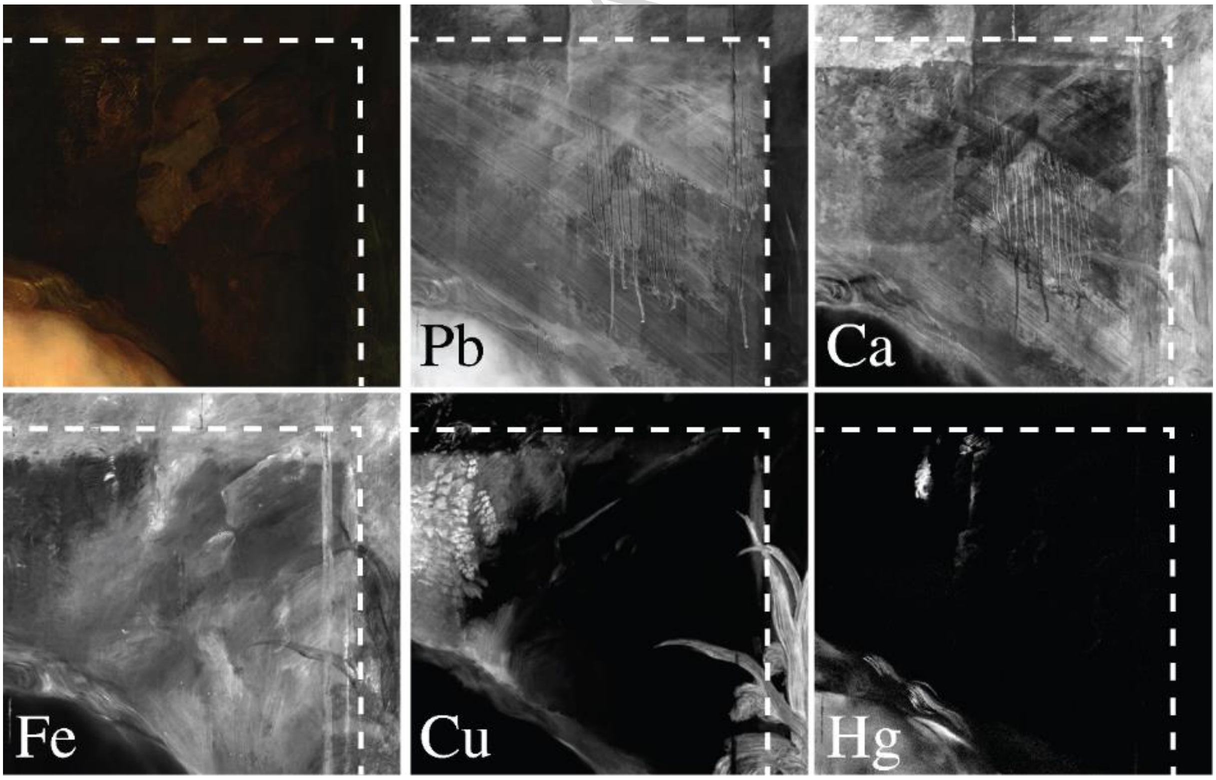

Figure 3: A detail of *Venus Frigida*, area indicated in Fig. 2, and the corresponding Pb (0-6900 counts), Ca (0-2100 counts), Fe (0-3800 counts), Cu (0-8700 counts) and Hg (0-1300 counts) distribution images (Map size 460 x 470 mm², step size 750 µm, 200 ms/pixel). The white dotted line indicates the physical edge of the centre piece.

Interestingly, Rubens' characteristic imprimatur is absent in the extensions around the centre piece. In this way, MA-XRF scanning signals a paint built-up that is deviant from the surrounding boards, confirming the hypothesis that these were not added by the master himself, but in a later stage. This is confirmed by numerous technical dissimilarities between the centre piece and the extensions that can be distinguished in the elemental images. The most striking differences are highlighted here such as the intensive use of smalt in the appended landscape (see Co map in Fig. 2) while this powdered blue glass pigment is absent in the nucleus panel. Also, Rubens recurred to vermillion (HgS) for the red cloth that lies at the feet of the Venus, whereas a hematite-based red earth was applied in the part that runs onto the added board (see Hg and Fe map in Fig. 2). Finally, copper is an element of high abundancy in the dark background of the initial panel, while it is sparsely applied in the adjacent top addition (see Cu map in Fig. 3).

Upon comparing the calcium maps with the physical edge of the centre piece, indicated with a white dotted line in Figure 3, it becomes clear that a paint overlap was made after the boards were added in order to regain visual unity within this mosaic composition. In particular, the planks added on the top and right exhibit an elevated calcium signal in comparison with the centre piece (see Ca map in Figs 2 and 3). However, this comparatively calcium rich area does not end at the interface of the planks, but continues well on to the central panel. This finding suggests that a calcium rich priming was applied after the boards were added, partly running over the original paint of the nucleus panel. This overlap has a noticeable shielding effect on the underlying lead-based imprimatur and the green copper paint of the vegetation on the central panel as well (see Pb and Cu map in Figure 3). In a later stage, the area was worked up with relatively bristly applied earth pigments, as demonstrated by the iron map in Fig. 3, hence disclosing the interface to the naked eye.

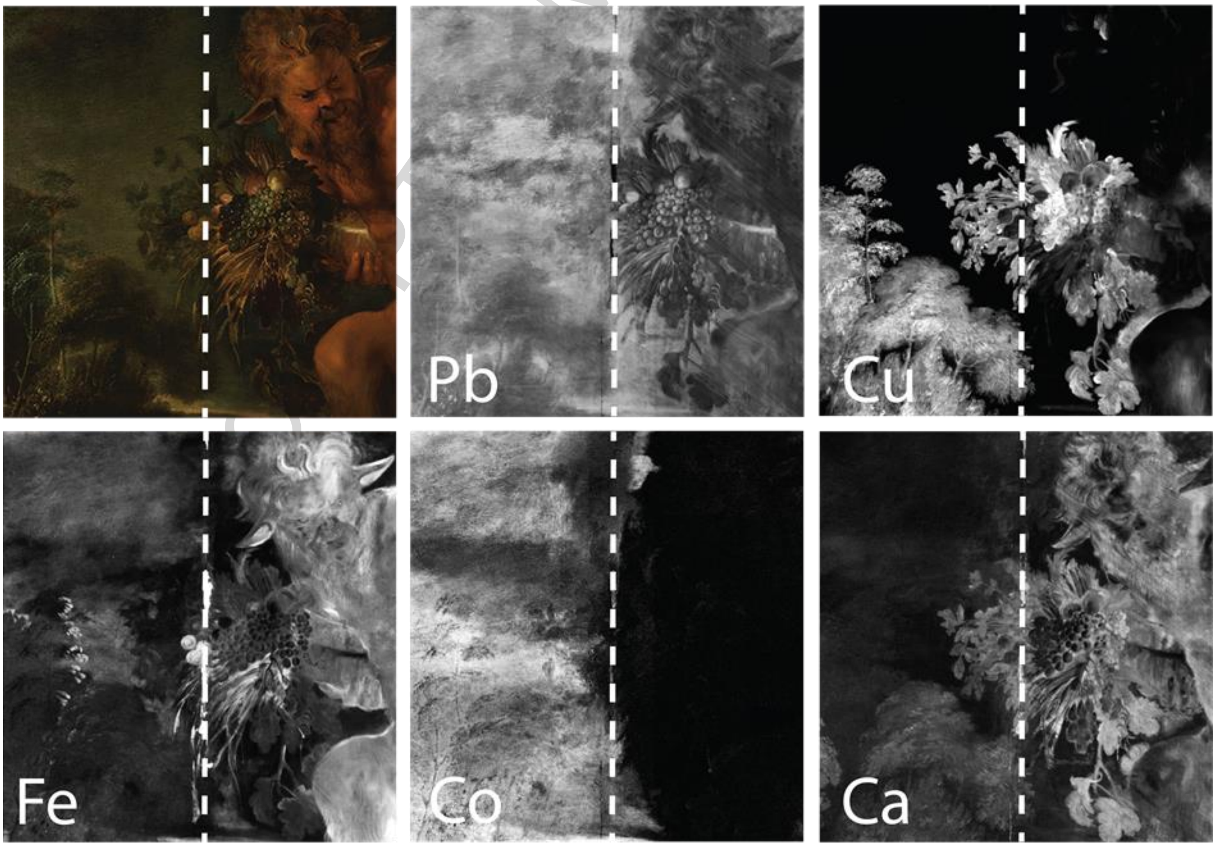

Figure 4: A detail of *Venus Frigida*, area indicated in Fig. 2, and the corresponding Pb (0-6500 counts), Cu (0-13100 counts), Fe (0-7300 counts), Co (0-680 counts) and Ca (0-1800 counts) distribution images (Map

size 510 x 490 mm², step size 750 µm, 200 ms/pixel). The white dotted line indicates the physical edge of the centre piece. Pb and Co image show how the paint of the landscape extension continues over the joint. In a second stage the horn and its content was enlarged onto the extension (Cu).

The complexity of this compound panel is further illustrated by the fact that the aforementioned overlap is not visible along the left edge. The different layer built-up along this left edge reflects the fact that the landscape was added in a separate phase, after the right and top additions. Here, the thick impasto paint of the landscape containing lead and cobalt (see fig $), runs over the joints, on to the original panel, attenuating the potential low-energetic signal of the underlying calcium priming. For the same reason, the horn that is held by the satyr appears differently on each side of the interface, when considering the elemental images in Figure 4. In particular, on the centre piece, the horn and its content seems reserved in the lead distribution, while its shape is barely visible on the extended part. When adding the landscape, the artist first applied the lead and cobalt-rich paint of the sky, slightly continuing onto the central panel where it was carefully applied around the horn. Afterwards, the copper-rich horn was extended onto the added landscape in order to obtain visual unity. As the emitted Pb and Co signals from the underlying sky are slightly shielded by the superimposed copper paint of the horn, the features of the horn emerge as faint 'shadows' in the lead and cobalt maps. More in general, the inferred stratigraphic variation between the left side versus top and right sides endorses the two-phased enlargement of the panel suspected by the conservators. Such comprehension of complex and varying layer sequences proved valuable during the conservation treatment that accompanied this research, in particular during the cleaning phase when decisions were made on the preservation or elimination of specific strata.

Figure 5: Detail of *Venus Frigida*, area indicated in Fig. 2. The copper map (0-13000 counts) and to a lesser extent the Pb map (0-7990 counts) shows a relative broad, subsurface band around the foot of the Venus (Map size 640x 660 mm², step size 750 µm, 200 ms/pixel).

A last intriguing feature, again related to Rubens' efficient technique, is the visualisation of broad contours around the incarnates (flesh tones). For instance, the elemental distribution images of lead and copper in Figure 5 unveil such a band around the foot of Venus and the backside of Amor. The 'halo' around the foot, indicated by a white arrow in Figure 5, is carefully applied along the outlines of the body parts but continues well under the adjacent textiles where it ends in a brushy manner. Similar dark contours have been found on other early paintings by Rubens as well, such as the Rockox triptych, discussed in the next paragraph.

Broad contours around the flesh tones of *The Incredulity of Saint Thomas* – 1613-'15

This altar piece (collection KMSKA, inv. no. 307-311) shown in Figure 6 was commissioned by Nicolaas II Rockox, mayor of Antwerp and his wife Adriana Perez. This so called 'Rockox triptych' was created around the same time as *Venus Frigida*, in a period during which Rubens exhibited unparalleled brushwork in the flesh tones, adulated by scholars with terms as 'polished' and 'mother-of-pearl' [15]. The MA-XRF maps collected on one of the hands of the dramatis personae is shown in Figure 6 for comparative reasons. A broad outline, similar to the halos found in the Venus painting (see Figure 5), shows up in the copper map around the fingers of the hand. This outline emerges faintly in the Pb image as well, next to the already discussed streaky imprimatur and a pentimento in the (elongated) thumb. The dark tone of the underlying outline currently contributes considerably to the colour observed at the surface, but the visual effect was probably originally less pronounced as the surface paint has partially lost its colour and lead soap formation is known to increase the transparency of superimposed paint strata with time [26].

There is still some debate on their function, but it is currently assumed that these dark halos were applied to locally emphasize the contrast between the luminous flesh tones and the darker textiles [15]. Interestingly, the distribution plot in Figure 6 shows that this copper pigment is only present along the top part of the hand, while the IRR exposes an outline along the entire hand, a contrast that is indicative of a carbon-based pigment. This finding suggests the use of a (variable) paint mixture containing a lead-, copper- and carbon-based pigments.

This practice is in line with the prevailing paint theory stating that surface colours should be strengthened with a (complimentary) coloured underpainting, while placing darker tones adjacent to lighter areas is a standard technique to enhance depth in a composition. However, Rubens seems to combine and bend these concepts to his economic method of working by applying this underpainting only where it is most needed, i.e. in interface areas where the colours directly meet incarnations [15]. In this way, Rubens draws the attention of the beholder to the virtuous paint handling of the flesh tones and at the same time enhances the sense of depth in the composition with the minimal effort of a few darker brush strokes. These halos seem related to Rubens early works, executed in a 'sculptural' style, the bands seem absent in his later work that is typified by a more suggestive way of painting.

Figure 6: Top: ***The Incredulity of Saint Thomas*** **by P.P. Rubens, 1613-'15, Royal Museum of Fine Arts Antwerp, inv. no. 307-311. © KMSKA - Lukas-Art in Flanders vzw. Photo Rik Klein Gotink. The white rectangle indicates the detail shown below (MA-XRF map size 280 x 300 mm², step size 850 µm, 200 ms/pixel). Middle: detail of a hand with corresponding IRR and XRR by Adri Verburgh, Arcobalena vzw. Below: MA-XRF maps of Cu (0-3700 counts), Pb (0-4200 counts) and Hg (0-1550 counts).**

Conclusions

The three case studies discussed in this paper illustrate how the hyperspectral method of MA-XRF scanning offers new avenues for non-invasive and comparative study of Rubens' painting practices and the identification of the applied materials. The added value in comparison with standard non-invasive imaging techniques was illustrated and mainly resides with the improved selectivity for studying the superimposed strata, a property that leads to a more comprehensive and cleaner documentation of Rubens' efficient and unbound painting practice. Nevertheless, it is clear that MA-XRF scanning does not render conventional IRR and XRR obsolete as the results appeared highly complementary. For instance, MA-XRF imaging on *Portrait of Hélène Fourment* granted full access to the animated background behind the sitter, an insight that was impossible to obtain by IRR and XRR due to an unfavourable combination of materials and build-up. On the other hand, IRR yielded more complete information with respect to the broad contours around the hand of Saint-Thomas, but MA-XRF revealed more details on its (variable) paint composition. For *Venus Frigida* the visualisation of various technical differences between the center piece and additions provided additional arguments for situating the extensions outside Rubens' studio. In view of its non-invasive aspect, this chemical imaging method also contributes significantly to the ongoing tendency in heritage science to prevent and/or to confine the extraction of sample material to an absolute minimum. Finally, the fact that chemical data can be acquired by spectroscopic analysis from the entire surface and presented in the form of comprehensible images enhances the significance of chemical analysis for art historical scholars and conservators.

Acknowledgements

This research was supported by the Baillet Latour fund. The staff of the Royal Museum of Fine Arts of Antwerp and the Kunsthistorisches Museum Wien are acknowledged for this pleasant collaboration and their authorisation for publication of the images in this article. Therefore, a word of gratitude to general director Manfred Sellink and director of collections Elsje Janssen of the KMSKA and their collaborators Johan Willems, Gwen Borms, Lies Vanbiervliet, Madeleine ter Kuile and Greta Toté. In addition, the authors would like to thank photographers Rik Klein Gotink and Adri Verburgh for kindly supplying the IRR and XRR images.

References

1. Janssens, K., et al., *The Use of Synchrotron Radiation for the Characterization of Artists' Pigments and Paintings*, in *Annual Review of Analytical Chemistry, Vol 6*, R.G. Cooks and J.E. Pemberton, Editors. 2013. p. 399-425.
2. Janssens, K., et al., *Non-Invasive and Non-Destructive Examination of Artistic Pigments, Paints, and Paintings by Means of X-Ray Methods.* Topics in Current Chemistry, 2016. **374**(6).
3. Van der Snickt, G., et al., *Material analyses of 'Christ with singing and music-making Angels', a late 15th-C panel painting attributed to Hans Memling and assistants: Part I. non-invasive in situ investigations.* Journal of Analytical Atomic Spectrometry, 2011. **26**(11): p. 2216-2229.
4. Shugar, A.N. and J.L. Mass, *Handheld XRF for art and archaeology*. Studies in archaeological sciences. 473 pages.
5. Alfeld, M., et al., *Optimization of mobile scanning macro-XRF systems for the in situ investigation of historical paintings.* Journal of Analytical Atomic Spectrometry, 2011. **26**(5): p. 899-909.
6. Romano, F.P., et al., *Real-time elemental imaging of large dimension paintings with a novel mobile macro X-ray fluorescence (MA-XRF) scanning technique.* Journal of Analytical Atomic Spectrometry, 2017. **32**(4): p. 773-781.
7. Alfeld, M., et al., *A mobile instrument for in situ scanning macro-XRF investigation of historical paintings.* Journal of Analytical Atomic Spectrometry, 2013. **28**(5): p. 760-767.
8. Van der Snickt, G., et al., *James Ensor's pigment use: artistic and material evolution studied by means of portable X-ray fluorescence spectrometry.* X-Ray Spectrometry, 2010. **39**(2): p. 103-111.
9. van Loon, A., et al., *Artificial orpiment, a new pigment in Rembrandt's palette.* Heritage Science, 2017. **5**.
10. Centeno, S.A., et al., *Van Gogh's Irises and Roses: the contribution of chemical analyses and imaging to the assessment of color changes in the red lake pigments.* Heritage Science, 2017. **5**.
11. Martins, A., et al., *Jackson Pollock's Number 1A, 1948: a non-invasive study using macro-x-ray fluorescence mapping (MA-XRF) and multivariate curve resolution-alternating least squares (MCR-ALS) analysis.* Heritage Science, 2016. **4**.
12. Dredge, P., et al., *Mapping Henry: Synchrotron-sourced X-ray fluorescence mapping and ultra-high-definition scanning of an early Tudor portrait of Henry VIII.* Applied Physics a-Materials Science & Processing, 2015. **121**(3): p. 789-800.
13. Van der Snickt, G., et al., *Large-Area Elemental Imaging Reveals Van Eyck's Original Paint Layers on the Ghent Altarpiece (1432), Rescoping Its Conservation Treatment.* Angewandte Chemie-International Edition, 2017. **56**(17): p. 4797-4801.
14. Alfeld, M. and J.A.C. Broekaert, *Mobile depth profiling and sub-surface imaging techniques for historical paintings - A review.* Spectrochimica Acta Part B-Atomic Spectroscopy, 2013. **88**: p. 211-230.
15. Hout, N.v. and A. Balis, *Rubens doorgelicht : meekijken over de schouder van een virtuoos*. 2010, Antwerp: Ludion : Koninklijk Museum voor Schone Kunsten. 168 p.
16. Sole, V.A., et al., *A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra.* Spectrochimica Acta Part B-Atomic Spectroscopy, 2007. **62**(1): p. 63-68.
17. Alfeld, M. and K. Janssens, *Strategies for processing mega-pixel X-ray fluorescence hyperspectral data: a case study on a version of Caravaggio's painting Supper at Emmaus.* Journal of Analytical Atomic Spectrometry, 2015. **30**(3): p. 777-789.
18. Van Espen, P., K. Janssens, and J. Nobels, *AXIL-PC, software for the analysis of complex X-ray spectra.* Chemometrics and Intelligent Laboratory Systems, 1986. **1**(1): p. 109-114.
19. Eastaugh, N., *The pigment compendium : a dictionary of historical pigments*. 2004, Amsterdam ; Boston: Elsevier Butterworth-Heinemann. xi, 499 p.
20. Van der Stighelen, K., *Helena Fourment further uncovered, A new interpretation of 'Het Pelsken' based on recent analytical imaging*, in *Rubens in private : the master portrays his family*, B. Van Beneden, Editor. 2015, Thames & Hudson, London: London. p. 76-97.
21. Gruber, G., *Rubens' Portrait of Helena Fourment, Hidden Aspects of the Fur*, in *Point of View: Unusual Insights into the Picture Gallery*. 2015, Kunsthistorishes Museum Wien: Vienna.
22. Poll-Rommel, V., *Anstückungen bei Tafelgemälden von Peter Paul Rubens Technik und Ausführung.* Restauro, 2001. **6**: p. 432-437.

23. Renger, K. *Anstückungen bei Rubens*. in *Die Malerei Antwerpens: Gattungen, Meister, Wirkungen: Studien zur flämischen Kunst des 16. und 17. Jahrhunderts, Internationales Kolloquium*. 1993. Wien: Locher Verlag.
24. Dubois, H. *Between creativity and economy: remarks on Rubens panel supports in the Royal Museums of Fine Arts of Belgium*. in *Studying Old Master Paintings. Technology and Practice, Postprints of the National Gallery Technical Bulletin 30th Anniversary Conference*. 2009. London: National Gallery.
25. Van Hout, N., *Meaning and development of the ground layer in seventeenth century painting*, in *Looking through paintings: the study of painting techniques and materials in support of art historical research*, E. Hermens, Editor. 1998, Prom: Baarn. p. 199-225.
26. Keune, K. and J.J. Boon, *Analytical imaging studies of cross-sections of paintings affected by lead soap aggregate formation.* Studies in Conservation, 2007. **52**(3): p. 161-176.

Highlights

- MA-XRF scanning proves a valuable, non-invasive tool for the comparative, technical study of P.P. Rubens painted oeuvre,
- MA-XRF imaging reveals hidden features of particular interest to scholars such as changes to the composition, extension of the wooden support and contrasting outlines around the flesh tones.
- Three case studies demonstrate the added value of elemental imaging in comparison with standard imaging techniques used for these purposes, i.e. X-ray radiography and Infrared Reflectography,
- Insights in the complex multi-layered build-up limit/prevent extraction of samples.